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Differential and integral cross sections for the rotationally inelastic scattering of methyl radicals with \( \text{H}_2 \) and \( \text{D}_2 \)

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Comparisons are presented of experimental and theoretical studies of the rotationally inelastic scattering of CD\(_3\) radicals with \( \text{H}_2 \) and \( \text{D}_2 \) collision partners at respective collision energies of 680 ± 75 and 640 ± 60 cm\(^{-1}\). Close-coupling quantum-mechanical calculations performed using a newly constructed \textit{ab initio} potential energy surface (PES) provide initial-to-final CD\(_3\) rotational level \((n, k \rightarrow n', k')\) integral and differential cross sections (ICSs and DCSs). The DCSs are compared with crossed molecular beam and velocity map imaging measurements of angular scattering distributions, which serve as a critical test of the accuracy of the new PES. In general, there is very good agreement between the experimental measurements and the calculations. The DCSs for CD\(_3\) scattering from both \( \text{H}_2 \) and \( \text{D}_2 \) peak in the forward hemisphere for \( n' = 2-4 \) and shift more to sideways and backward scattering for \( n' = 5 \). For \( n' = 6-8 \), the DCSs are dominated by backward scattering. DCSs for a particular CD\(_3\) \( n \rightarrow n' \) transition have a similar angular dependence with either \( \text{D}_2 \) or \( \text{H}_2 \) as collision partner. Any differences between DCSs or ICSs can be attributed to mass effects because the PES is unchanged for CD\(_3\)-\( \text{D}_2 \) and CD\(_3\)-\( \text{D}_2 \) collisions. Further comparisons are drawn between the CD\(_3\)-\( \text{D}_2 \) scattering and results for CD\(_3\)-He presented in our recent paper.[O. Tkáč, A. G. Sage, S. J. Greaves, A. J. Orr-Ewing, P. J. Dagdigian, Q. Ma, and M. H. Alexander, Chem. Sci. 4, 4199 (2013)]. These systems have the same reduced mass, but are governed by different PESs. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4879618]

I. INTRODUCTION

The potential energy surface (PES) is a key theoretical concept in the field of molecular reaction dynamics.\(^1\) Modern quantum chemistry provides methods to compute \textit{ab initio} PESs within the Born-Oppenheimer approximation, while measurement of state-to-state differential cross sections (DCSs) provide an excellent experimental test of the accuracy of the PES since the DCSs are sensitive to both attractive and repulsive parts of the potential.\(^2\) The accuracy of a computed PES can hence be tested by comparing theoretical DCSs, calculated from quantum scattering theory, with experimentally measured DCSs. If theory and experiment are found to be in good agreement, robust deductions can be drawn about the collision dynamics, including the relationship between experimental measurables (e.g., angular distributions and state propensities) and features of the PES controlling the collision dynamics.

We focus here on DCSs involving the inelastic scattering of methyl radicals with molecular hydrogen. Studies of collisions of several important species (e.g., \( \text{H}_2\text{O}, \text{OH}, \text{NH}_3, \) and \( \text{CH}_4 \)) with molecular hydrogen are motivated by astrophysical applications, because of the high abundance of \( \text{H}_2 \) in the universe. Collisions involving methyl radicals are of particular interest for the hydrocarbon chemistry of the atmospheres of the outer planets in the solar system,\(^3–\text{5}\) as well as Titan.\(^6\) Methyl radical chemistry is important in the combustion of hydrocarbons\(^7,\text{8}\) and chemical vapour deposition of diamond films.\(^9,\text{10}\) In addition, methyl radicals may be an integral part of a catalytic cycle for partial oxidation of methane to formaldehyde or methanol for chemical feedstocks.\(^11\)

From a theoretical perspective, accurate close-coupling DCSs for methyl scattering are computationally tractable for collisions involving the \( \text{H}_2 \) or \( \text{D}_2 \) molecule because their large rotational constants \([B(\text{H}_2) = 60.853 \text{ cm}^{-1}\) and \( B(\text{D}_2) = 30.443 \text{ cm}^{-1}\)]\(^12\) mean that only a few rotational levels of the collision partner need to be included in quantum scattering calculations. Although \( \text{D}_2 \) has the same mass as a He atom, collisions involving the diatomic molecule can change the internal state of both collision partners, along with the relative kinetic energy. Comparison of inelastic DCSs for collisions of methyl radicals with He, \( \text{H}_2 \), and \( \text{D}_2 \) might therefore distinguish the consequences of the additional molecular rotational degrees of freedom from purely mass related effects.

The inelastic scattering of labile free radicals was extensively reviewed in the mid 1990s,\(^13–\text{15}\) with a focus on state-resolved integral cross sections (ICSs). Since then, experimental studies using velocity map imaging (VMI)\(^16,\text{17}\) and laser spectroscopic detection have revolutionized...
measurement of state-resolved DCSs, for which the most extensively studied molecules are the NO\textsuperscript{18–26} or OH\textsuperscript{27–35} diatomic radicals. To date, the only reported measurement of DCSs for inelastic scattering of polyatomic free radicals is our recent study of methyl radical scattering by He.\textsuperscript{36} We found excellent agreement between experimental measurements and DCSs calculated using the recent PES of Dagdigian and Alexander.\textsuperscript{37} The inelastic scattering of closed-shell polyatomic molecules is more extensively illustrated by determinations of DCSs for scattering of ammonia\textsuperscript{38–40} and deuterated ammonia\textsuperscript{41,42} with rare gases and molecular hydrogen, and for water with helium\textsuperscript{35} and hydrogen.\textsuperscript{44} The rotationally inelastic scattering of deuterated methyl radicals and ammonia in collisions with helium were recently compared, using close-coupling quantum-mechanical scattering calculations performed with accurate \textit{ab initio} PESs.\textsuperscript{45}

Dagdigian’s review of quantum scattering calculations of collisional energy transfer in small hydrocarbon intermediates provides a current perspective on polyatomic radical scattering\textsuperscript{46} and highlights studies involving methylene (CH\textsubscript{2})\textsuperscript{47,48} and methyl\textsuperscript{37,49,49} The energy transfer dynamics for a polyatomic species like the methyl radical are more complicated than for collisions of a diatomic molecule with an atom. In the latter case, the cylindrical symmetry limits the anisotropy to that associated with the polar angle away from the molecular axis. In contrast, for collisions of methyl radicals, anisotropies must be considered that are associated with the polar angle (away from the C\textsubscript{3} symmetry axis) and the azimuthal angle about this axis.

In the work reported here, DCSs for collisions of CH\textsubscript{3} and CD\textsubscript{3} with H\textsubscript{2} and D\textsubscript{2} were experimentally determined using crossed molecular beam (CMB) and VMI methods. However, we concentrate on the DCSs for collisions of CD\textsubscript{3} since only a few CH\textsubscript{3} levels can be cleanly detected because of predissociation of the excited-state used for spectroscopic detection. We compare the measured DCSs with results from quantum close-coupling scattering calculations performed using a newly computed \textit{ab initio} PES.

II. METHOD

A. Experimental apparatus

The compact crossed molecular beam apparatus used for measurement of DCSs was described in detail previously,\textsuperscript{36} and we present only a brief summary of the experimental method here. Schematic top and side views of the instrument were shown in Fig. 1 of Ref. 36. Molecular beams were formed by supersonic expansion through a pair of pulsed valves (General Valve Series 9) and were collimated by skimmers. The methyl radical primary molecular beam was formed by 266 nm photolysis of CH\textsubscript{3}I or CD\textsubscript{3}I in 3\% mixtures in Ar, at a stagnation pressure of 4 bar, immediately after the orifice of the pulsed valve. The secondary molecular beam was formed by expansion of 4 bar of pure D\textsubscript{2} or H\textsubscript{2}. The two skimmed beams propagated horizontally and crossed at a 90\degree intersection angle in a high vacuum scattering chamber. A typical base pressure for the scattering chamber was \(<10^{-5}\) Torr with the pulsed valves turned off, and this rose to \(\sim 10^{-7}\) Torr when the valves were operating.

The intersection region of the two molecular beams was located within a vertically mounted stack of 20 electrodes forming an ion optics assembly for dc slice-imaging.\textsuperscript{50} A probe laser focused to the intersection of the beams ionized the scattered methyl radicals, and the electric field created by the electrode stack accelerated the ions upwards towards a position-sensitive detector. The ion detector (Photek) consisted of a pair of microchannel plates (MCPs), a phosphor screen (P46 phosphor) and a CCD camera. The voltage applied to the rear MCP was pulsed for 20 ns to time-gate the detection of ions.

UV radiation in the wavelength range 285–288 nm required for (2+1) resonance enhanced multiphoton ionization (REMPI) detection of the methyl radicals was generated by frequency doubling the output of a tuneable pulsed dye laser. The energy and linewidth of the probe laser beam were 4.5 mJ/pulse and 0.0027 nm (0.32 cm\textsuperscript{-1}), respectively. In our experiments, the maximum Doppler shift of inelastically scattered CD\textsubscript{3} radicals was 0.12 cm\textsuperscript{-1}, which is smaller than the laser linewidth. Methyl radicals were therefore ionized using fixed laser wavelengths chosen to probe particular rotational levels.

The electrodes forming the homogeneous acceleration field stretched the methyl ion packet along the flight axis according to the initial velocities of the neutral methyl radicals. The short voltage pulse applied to the rear MCP then allowed only a thin central slice of the ion packet to be recorded, corresponding to methyl radicals scattered within, or close to the plane of the crossed molecular beams. Direct analysis of this slice image gave the three-dimensional velocity distribution of the inelastically scattered methyl radicals without the need for image reconstruction techniques. The nozzle producing the secondary beam of pure hydrogen was operated in a repeating mode of 50 shots on and 50 shots off. The desired scattering signal was than obtained by subtraction of the background (without H\textsubscript{2}/D\textsubscript{2}) image from the total signal image.

Analysis of experimental images required a density-to-flux transformation because the detection efficiency of the scattered products depended on their laboratory frame velocity. To correct the images for this detection bias, we employed the method of Monte Carlo simulation of the experiment as described previously,\textsuperscript{36} using a modification of the computer program of Eyles and Brouard.\textsuperscript{51} Further details of the density-to-flux transformation can be found in the supplementary material.\textsuperscript{52} Low signal levels prevented any study of laboratory-frame angular momentum polarization of the scattered methyl radicals.

B. REMPI detection and state distribution in incident beams

The methyl radical is an oblate symmetric top, with rotations described by total rotational angular momentum \(n\) and its body-frame projection \(k\). The fine-structure and hyperfine splittings are very small\textsuperscript{53} and are ignored in our theoretical treatment. As discussed in detail previously,\textsuperscript{36} the CH\textsubscript{3} and...
CD$_3$ radicals exist in two and three nuclear spin modifications, respectively, that do not interconvert in molecular collisions. The energies of low-lying rotational levels of CH$_3$ and CD$_3$ have been plotted in Fig. 3 of Ref. 36. The normal forms (statistical mixtures of ortho and para modifications) of the H$_2$ and D$_2$ collision partners were employed in the scattering experiments.

The rotational level populations in the incident radical beam and the inelastically scattered CD$_3$ or CH$_3$ final levels were determined using (2+1) REMPI spectroscopy through the 0$_0^+$ band of the $4p^2 A^+$$_2 \leftarrow X^2 A^+_2$ transition. The level distributions in the incident radical beams were determined by comparison of experimental spectra with spectra simulated using the PGOPHER program. As was shown in our recent paper, the methyl radicals cooled to a rotational temperature of ~15 K. The relative populations of the rotational levels were presented in Table 1 of Ref. 36.

The lines in the REMPI spectrum of methyl are resolved in the $n$ rotational quantum number, but not in the $\Lambda$ projection quantum number. Depending upon the spectroscopic branch (hence $\Delta n$ of the transitions), the $\Lambda$ projection levels of a given $n$ contribute differently. The levels associated with the DCSs reported below are denoted by $n_1$, $n_2$, $\ldots$ levels have been detected on a given transition. The relative contributions of the different $k$ projection levels to the measured REMPI intensity were determined by calculating 2-photon line strength factors using the PGOPHER program.

The levels of the excited $4p^2 A^+$$_2$ electronic state are pre-dissociated, and the linewidths for the CH$_3$ isotopologue are larger than for CD$_3$. Hence, the efficiency of detection of CH$_3$ rotational levels is lower, and DCSs were determined for fewer final levels than for CD$_3$. For this reason, we concentrate in this paper on the DCSs for CD$_3$ collisions and experimental images and DCSs for CH$_3$ radical can be found in the supplementary material.

C. Potential energy surface

The geometry of the CH$_3$–H$_2$ rigid-rotor complex can be described by six coordinates, similar to those used in earlier work by Rist et al. on the NH$_3$–H$_2$ system. These include the intermolecular separation $R$ and four angles $(\theta_1, \phi_1)$ and $(\theta_2, \phi_2)$ describing the orientations of the CH$_3$ and H$_2$ collision partners, respectively, relative to the Jacobian vector connecting the two molecules. This body-frame coordinate system is illustrated in Fig. 1.

In order to determine the form of the angular dependence of the potential, we follow the work by Rist et al. and consider the interaction of a symmetric top with a linear molecule as the expectation value of the sum of electrostatic interactions between the two molecules:

$$V = \langle \psi_1 \psi_2 | V | \psi_1 \psi_2 \rangle = \langle \psi_1 \psi_2 \rangle \sum_{ij} q_i q_j r_{ij}^{-1} | \psi_1 \psi_2 \rangle,$$

where $\psi_1$ and $\psi_2$ are the electronic wave functions of the two molecules and $q_i$ is the charge of particle $i$. The inverse separation between a pair $ij$ of electrons can be expressed as a triple sum of modified spherical harmonics:

$$r_{ij}^{-1} = \sum_{l_1 l_2} A_{l_1 l_2 j} (r_1, r_2, R) \times \sum_{m_1 m_2 m} (l_1 m_1 l_2 m_2 | l m) C_{l_1 m_1} (\hat{r}_1) C_{l_2 m_2} (\hat{r}_2) C_{l m}^* (\Omega_{BS}).$$

In Eq. (2), $r_1$ and $r_2$ are the space-fixed coordinates of the $i$th and $j$th particles of molecules 1 and 2, respectively, relative to the center of mass of each molecule. The term $(l_1 m_1 l_2 m_2 | l m)$ is a Clebsch-Gordan coefficient, the $C_{l m}$ are modified spherical harmonics, and $\Omega_{BS}$ is the orientation of the body frame with respect to the space frame. For non-overlapping charge distributions, we must have $l = l_1 + l_2$; however, $l$ can have the full range $|l_1 - l_2| \leq l \leq l_1 + l_2$ for overlapping distributions, as would be the case for an intermolecular potential.

We transform the first two spherical harmonics to the body frame

$$C_{l_1 m_1} (\hat{r}_1) = \sum_{\mu_1} D_{l_1 m_1 \mu_1}^* (\Omega_{1S}) C_{l_1 \mu_1} (\hat{\rho}_1),$$

and similarly for molecule 2. Substitution of Eqs. (2) and (3) into Eq. (1) and integration over the electronic coordinates yields the following formal expression for the interaction potential:

$$V(R, \Omega_{1S}, \Omega_{2S}) = \sum_{l_1 l_2 \mu_1 \mu_2} B_{l_1 l_2 \mu_1 \mu_2} (R) \sum_{m_1 m_2 m} (l_1 m_1 l_2 m_2 | l m) \times \sum_{\mu_1} D_{l_1 m_1 \mu_1}^* (\Omega_{1S}) D_{l_2 m_2 \mu_2}^* (\Omega_{2S}) C_{l m}^* (\Omega_{BS}).$$

In Eq. (4), the $B$ terms are radial expansion coefficients, and the $D_{l m \mu}^*$ are rotation matrix elements. Since $V$ is independent of the choice of the space frame, we align the space frame with the body frame (i.e., we align $R$ along the space frame $z$ axis). In this case, only $m = 0$ terms contribute to the potential. Also, only $\mu_2 = 0$ terms contribute since the electronic wave function of H$_2$ is cylindrically symmetric. From Fig. 1, we define the orientation between CH$_3$ and H$_2$ as follows:
\[ \Omega_{B1} \equiv (\phi_1, \theta_1, 0) \text{ defines the Euler angles to rotate the CH}_3 \text{ molecule frame to the body frame, and } \Omega_{B2} \equiv (\phi_2, \theta_2, 0) \text{ rotates the body frame to the H}_2 \text{ molecule frame. With these considerations, we can rewrite Eq. (4) as} \]

\[
V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_1, \mu_1 \geq 0} B_{l_1, \mu_1}(R) \left( \sum_{m_1} (l_1 m_1 | l_2, -m_1 | 0) \right) \times D_{\mu_1 \mu_1}^{l_1 \ast}(0, -\theta_1, -\phi_1) D_{-\mu_1 \mu_1}^{l_2}(\phi_2, \theta_2, 0).
\]

(5)

Symmetry considerations restrict the allowed terms in Eq. (5). The threefold symmetry of \( \text{CH}_3 \) requires that \( \mu_1 \) be a multiple of 3. The potential is invariant to exchange of the hydrogen nuclei in \( \text{H}_2 \), hence \( l_1 \) must be even. Since \( V \) is real, it can be shown that

\[
B_{l_1, \mu_1}(R) = (-1)^{l_1+l_2+l+\mu_1} B_{l_1, -\mu_1}(R).
\]

(6)

Since \( V \) must be invariant to reflection of \( \text{H}_2 \) through the \( xz \) plane of the \( \text{CH}_3 \) molecule frame, we have

\[
B_{l_1, l_2, -\mu_1}(R) = (-1)^{l_1+l_2+l+\mu_1} B_{l_1, l_2, \mu_1}(R).
\]

(7)

Equations (6) and (7) imply that the \( B \) coefficients in Eq. (5) are real. In addition, \( V \) is invariant to reflection of \( \text{H}_2 \) through the \( xy \) plane of the \( \text{CH}_3 \) molecule frame since \( \text{CH}_3 \) is planar. It can be shown that this property restricts \( l_1 + l + \mu_1 \) to be even. The potential should also be invariant with respect to inversion of all coordinates; this parity invariance restricts the \( l_1 + l + l \) to even values.\(^{67}\) However, this symmetry can be broken for the interaction of a nonlinear molecule with a diatomic.\(^{61,62}\)

Substituting Eq. (7) into Eq. (5) and resolving the rotation matrix elements in Eq. (5) into products of complex exponentials and reduced rotation matrix elements, \( d_{\mu m}^{l} \), we obtain

\[
V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_1, l_2, \mu_1 \geq 0} B_{l_1, l_2, \mu_1}(R) \left( 1 + \delta_{\mu_1, 0} \right) \sum_{m_1} (l_1 m_1 | l_2, -m_1 | 0) \times \left[ e^{-i\mu_1 \phi_1} d_{\mu_1 m_1}^{l_1}(\theta_1) + (-1)^{l_1+l_2+l+\mu_1} e^{i\mu_1 \phi_1} d_{\mu_1 m_1}^{l_1}(\theta_1) \right] e^{-i m_1 \phi_2} d_{l_2, m_1}^{l_2}(\theta_2).
\]

(8)

The PES was fitted with a modified version of Eq. (8),

\[
V(R, \theta_1, \phi_1, \theta_2, \phi_2) = \sum_{l_1, l_2, \mu_1 \geq 0} C_{l_1, l_2, \mu_1}(R) \frac{\left( l_1 \right| l_2 \right)}{2 \pi} \left( \frac{l_1 \| l_2 \|}{2} \right)^{1/2} \times \sum_{m_1 \geq 0} (1 + \delta_{m_1, 0})^{-1} (l_1 m_1 | l_2, -m_1 | 0) d_{m_1, 0}^{l_2}(\theta_2) \times \cos(\mu_1 \phi_1 + m_1 \phi_2) d_{\mu_1 m_1}^{l_1}(\theta_1) + (-1)^{l_1+l_2+l+\mu_1} \cos(\mu_1 \phi_1 - m_1 \phi_2) d_{\mu_1 m_1}^{l_1}(\theta_1),
\]

(9)

where \( [x] = 2x + 1 \) and

\[
C_{l_1, l_2, \mu_1}(R) = \frac{4\pi}{1 + \delta_{\mu_1, 0}} \left( \frac{2}{l_1 \| l_2 \|} \right)^{1/2} B_{l_1, l_2, \mu_1}(R).
\]

(10)

The angular expansion in Eq. (9) is normalized so that the significance of individual terms can be evaluated directly.

We performed the explicitly correlated restricted coupled-cluster calculations with full inclusion of single and double excitations and perturbative inclusion of triple excitations \([\text{RCCSD(T)}-\text{F12a}]\)\(^{63,64}\) of the \( \text{CH}_3-\text{H}_2 \) PES. We employed the aug-cc-pVTZ correlation-consistent basis sets,\(^{65,66}\) with aug-cc-pVTZ/MP2FIT and cc-pVTZ/JKFIT as the density fitting basis and the resolution of identity basis, respectively.\(^{67,68}\) A counterpoise correction was applied to correct for basis-set superposition error.\(^{69}\) All calculations were carried out with the MOLPRO 2010.1 suite of programs.\(^{70}\)
of the average of the absolute value $|V|$ of the potential for $R \geq 4.75$ bohr $|V| = 2500$ cm$^{-1}$. Using the Monte Carlo error estimator,\textsuperscript{35} we found the norm $\|S^{-1}\|$ for our randomly generated orientations and angular basis is 1.52. A value of $\|S^{-1}\|$ close to 1 indicates sufficient angular sampling.

Figure 2 presents a plot of the larger expansion coefficients $C_{l_1l_2l_3}(R)$ as a function of the intermolecular separation $R$ in the region of the van der Waals well. For the terms involving the interaction with spherically averaged H$_2$ (i.e., $l_2 = 0$), shown in the upper panel of Fig. 2, the largest coefficients are the same as for CH$_3$–He,\textsuperscript{37} namely $(l_1, \mu_1) = (3, 3)$ and $(2, 0)$. These reflect the leading anisotropies involving approach of the collision partner within and perpendicular to the plane of the methyl radical, as discussed previously for CH$_3$–He.\textsuperscript{37} The lower panel of Fig. 2 displays the larger $C_{l_1l_2l_3}(R)$ coefficients with $l_2 = 2$, which reflect the molecular nature of the collision partner. The plotted coefficients are direct analogs of the $l_2 = 0$ coefficients plotted in the upper panel, namely $(l_1, \mu_1) = (0, 0), (3, 3), (2, 0)$, and $(5, 3)$, with $l = l_1 + l_2$.

The global minimum of the PES has $D_e = 99.0$ cm$^{-1}$, at a geometry of $R = 6.57$ bohr, $\theta_1 = 0^\circ$, $\theta_2 = 0^\circ$ (the $\phi$ angles are meaningless here). The H$_2$ molecule thus lies along the $C_3$ axis of the methyl radical above (or below, by symmetry) the molecular plane. The well depth $D_e$ is therefore larger than that for CH$_3$–He [27.0 cm$^{-1}$ (Ref. 37)]. The equilibrium geometry differs from that of the global minimum for CH$_3$–He,\textsuperscript{37} for which the He atom lies in the molecular plane and bisects two C–H bonds.

Figure 3 presents contour plots of the dependence of the potential upon the orientation of the methyl radical for two orientations of H$_2$ for $R = 6.5$ bohr. For $\theta_2 = 0^\circ$ (left-hand panel of Fig. 3) the CH$_3$ orientation for the most attractive interaction is the same as that of the global minimum. In this case the maximum repulsion occurs for $\theta_1 = 90^\circ$ and $\phi_1 = 0^\circ$, $120^\circ$, $240^\circ$; this corresponds to approach of one end of the H$_2$ molecule in the CH$_3$ plane toward one of the C–H bonds. The right-hand panel of Fig. 3 displays a contour plot of the potential for $\theta_2 = 90^\circ$, $\phi_2 = 0^\circ$. In this case, the most attractive CH$_3$ orientation ($\theta_1 = 90^\circ$ and $\phi_1 = 60^\circ$, $180^\circ$, $300^\circ$) corresponds to approach of the center of the H$_2$ molecule in the molecular plane and bisecting two C–H bonds, with the H$_2$ internuclear axis lying perpendicular to the CH$_3$ plane. The new PES can be used without modification in scattering calculations on CD$_3$–H$_2$ and CD$_3$–D$_2$ collisions since the centers of mass are unaffected for both molecules upon isotopic substitution.

D. Quantum scattering calculations

State-to-state DCSs and ICSs for collisions of CD$_3$ with H$_2$ and D$_2$ were calculated using the HIBRIDON suite of programs\textsuperscript{73} and the PES described in Sec. II C. Rotational energies for CD$_3$ were computed with a rigid rotor symmetric top Hamiltonian using rotational constants from a spectroscopic study by Sears et al.\textsuperscript{74} Separate calculations were carried out for each nuclear spin modification of both CD$_3$ and H$_2$/D$_2$ since they are not interconverted in molecular collisions. The close-coupling channel basis consisted of CD$_3$ rotational levels whose energies were less than 960 cm$^{-1}$ and H$_2$/D$_2$ rotational levels with $j_2 \leq 2$, and the calculations included total angular momenta $J \leq 100$. Convergence of the DCSs to within $\sim 5\%$ was checked with respect to the size of the rotational basis and the number of partial waves in the calculation. The scattering calculations used up to 5366 channels.
Since the CD$_3$ incident beam contained several rotational levels, DCSs for formation of a specific final rotational level $n_f$ were determined by weighting the computed state-to-state DCSs at the experimental collision energy by the experimentally determined incident beam rotational level populations presented in Table 1 of Ref. 36. Since the $k$ projection number is not resolved in the REMPI spectra, computed DCSs for comparison with the experimental measurements were weighted according to the 2-photon line strengths factors for the given detection line. We assume the H$_2$/D$_2$ incident beam contains a statistical mixture of $j_2 = 0$ and 1 rotational levels and did not consider initial levels with $j_2 \geq 2$. The only $j_2$-changing transition included in our DCS calculations was $j_2 = 0 \rightarrow 2$. Including both the $j_2 = 0 \rightarrow 0$ and $j_2 = 0 \rightarrow 2$ transitions changes the averaged DCSs by $<10\%$ (except for $\theta < 20^\circ$), an angular range obscured by the incident beam), compared to including $j_2 = 0 \rightarrow 0$ transitions alone. We expect the DCSs of other $j_2$-changing transitions to be even less significant due to larger energy gaps.

In previous work, we examined propensities caused by the leading angular expansion coefficients of the PES in the ICSs for CH$_3$ and CD$_3$ transitions induced by collision with He. We briefly explore here these propensities for collisions of CD$_3$ with D$_2$. Figure 4 presents computed state-resolved ICSs for collision of the CD$_3$ 10 level, the lowest level of $A_1$ nuclear spin modification, with the D$_2$ $j_2 = 0$ and 1 rotational levels for which $j_2$ is the same after the collision. These cross sections were calculated for a collision energy of 640 cm$^{-1}$. ICSs for transitions out of the lowest rotational levels of the $A_2$ and $E$ nuclear spin modifications can be found in the supplementary material.

We see in Fig. 4 that for most CD$_3$ transitions the ICSs for $j_2 = 1$ are only slightly larger than for $j_2 = 0$. The major exception is for the $1_0 \rightarrow 3_0$ transition, for which the cross section for $j_2 = 1$ is $\sim70\%$ larger than for $j_2 = 0$, and this increase is seen in the DCS for $\theta \leq 45^\circ$. In some other molecule–H$_2$ systems, e.g., OH–H$_2$, H$_2$O–H$_2$, NH$_3$–H$_2$, the cross sections for the $j_2 = 1$ initial level are much larger than for $j_2 = 0$. In these systems, the collision partners of H$_2$ have nonzero dipole moments so that the leading electrostatic term is the dipole-quadrupole interaction. This interaction corresponds to the $l_1 = 1, l_2 = 2, l = 3$, terms and could contribute to the cross sections for the $j_2 = 1$ but not $j_2 = 0$ initial level. Since methyl has no dipole moment, this interaction is missing for CD$_3$–H$_2$/D$_2$. For both these systems, the transitions with the largest cross sections are to the 3$_1$ and 3$_0$ levels; the same propensities were found for collisions with He. These final levels are directly coupled by the $(l_1, \mu_1) = (3,3)$ and (2,0) terms, respectively, of the PES.

III. RESULTS

Newton diagrams for inelastic scattering of CD$_3$ with D$_2$ and H$_2$ are shown in Fig. 5 and illustrate the laboratory frame velocities of CD$_3$ [$v_{CD3} = 550 \pm 30$ m s$^{-1}$], D$_2$ and H$_2$ [$v(D_2) = 2090 \pm 210$ m s$^{-1}$ and $v(H_2) = 2950 \pm 320$ m s$^{-1}$], and the pre- and post-collision center-of-mass (CM) frame velocities of the methyl radical $u'(CD_3)$ and $u'(CD_3)$, respectively. The CM-frame scattering angle $\theta$ is defined as the angle between the CM-frame velocities of CD$_3$ before and after a collision. The displayed Newton spheres correspond to a CD$_3$ transition from initial level $n_k = 0_0$ into final level $n'_k = 2_0$, with an associated energy transfer of $\Delta E = 29$ cm$^{-1}$, and to $\Delta j_2 = 0$ and $j_2 = 0 \rightarrow j'_2 = 2$ transitions between rotational levels of D$_2$ and H$_2$. 

![FIG. 4. ICSs for transitions out of the CD$_3$ 10 level (the lowest level of the $A_1$ nuclear spin modification) in collisions with D$_2$ at a relative translational energy of 640 cm$^{-1}$. The rotational level of the collision partner is $j_2 = 0$ (upper panel) and $j_2 = 1$ (lower panel). The initial level is indicated with an open square. Since the cross sections for transitions to CD$_3$ high $n$ levels are small, the plots show cross sections for final levels with $n' \leq 10$.](image)

![FIG. 5. Newton diagrams for inelastic scattering of CD$_3$ with (a) D$_2$ and (b) H$_2$. The Newton spheres are drawn for inelastic scattering of CD$_3$ from the initial state $n_k = 0_0$ to the final state $n'_k = 2_0$, which corresponds to an energy transfer of $\Delta E = 29$ cm$^{-1}$ and for $\Delta j_2 = 0$ and $j_2 = 0 \rightarrow j'_2 = 2$ transitions between rotational levels of D$_2$ and H$_2$.](image)
FIG. 6. Raw images for inelastic scattering of CD₃ radicals by D₂ at a collision energy of 640 ± 60 cm⁻¹. The images are labelled by the symbol Y(n′,k′) for final rotational levels with n′ = 2–7 for the CD₃ radical, with unresolved final k′ projection levels as discussed in Sec. II B. Y denotes the spectroscopic branch. The orientation of the relative velocity vector v_rel is indicated in one panel.

Collision energies for inelastic scattering of CD₃ with D₂ and H₂ were 640 ± 60 and 680 ± 75 cm⁻¹, respectively. Figure 6 presents the raw images recorded for detection of CD₃ after collision with D₂. Raw images for detection of CD₃ after collision with H₂ can be found in the supplementary material.²² It should be noted that conservation of momentum during a collision implies that images for CD₃–H₂ scattering obtained from detection of the methyl radicals are smaller than for D₂ (and He) as a collision partner. The scattered products cannot be observed in the parts of the images closest to the forward direction because of imperfect subtraction of background signals arising from unscattered and incompletely cooled CD₃ radicals in the parent molecular beam. Asymmetry in the images about the relative velocity vector is a consequence of speed-dependent detection bias, as mentioned in Sec. II A, but is corrected for by density-to-flux transformation of the data.

In most cases, more than one spectroscopic branch was probed for a given final n′, giving different contributions of the unresolved k′ projections with weighting according to the 2-photon line strength factors, as discussed in Sec. II B. From examination of the images, we see that the scattering is confined relatively close to the incident beam direction because of imperfect subtraction of background signals arising from unscattered and incompletely cooled CD₃ radicals in the parent molecular beam. The method of normalization of the experimental DCSs is described in the main text.

The Newton diagrams shown in Fig. 5 demonstrate that the Newton spheres for the rotational transition of D₂ from j₂ = 0 to j₂′ = 0 and 2 would not be distinguishable in the measured images. Comparison of measured images for H₂ as a collision partner with the Newton diagram indicates that transitions involving rotational excitation of H₂ in a collision do not contribute significantly to the scattering, as also found in the scattering calculations (see Sec. II D). DCSs are different for a given final level n′ of CD₃ but various changes of the H₂ and D₂ rotational angular momentum; however, it is not possible to separate these types of Newton spheres from the measured images. The reason is that the experimental images result from superposition of many Newton spheres differing slightly in the magnitude and direction of the initial velocities of the collision partners and these Newton spheres are not perfectly concentric.

The recorded images were corrected with the density-to-flux transformation in order to derive the DCSs. Figure 7 displays the determined DCSs for CD₃–D₂ for final levels n′ = 2 – 4, while Fig. 8 presents the DCSs for n′ = 5 – 7. Also plotted in Figs. 7 and 8 are the theoretical DCSs. The experimental and calculated DCSs for the CD₃–H₂ system are shown in Fig. 8.
FIG. 8. Experimental (red) and theoretical (black) DCSs for inelastic scattering of CD$_3$ radicals by D$_2$ at a collision energy of 640 ± 60 cm$^{-1}$ into final rotational levels $n' = 5–7$. The REMPI line employed for detection is indicated, along with the range of $k'$ projection levels contributing to the scattering. The method of normalization of the experimental DCSs is described in the main text.

Fig. 9 for final levels $n' = 2–4$ and in Fig. 10 for $n' = 5–8$. For quantitative comparison with the theoretical calculations, the experimental DCSs were normalized by scaling the experimental value at 60° scattering angle to match the theoretical value at that angle. Since the scattering is mainly into the backward hemisphere for large $\Delta n$ transitions, the DCSs for the $R(7)$ and $P(8)$ lines for collision with H$_2$ were normalized at 90°.

The experimental DCSs are not shown for $\theta < 30°$ for final levels with $n' = 2$ and 3 and for $\theta < 20°$ for final levels with higher $n'$ because of contributions to these angles from unscattered radicals in the parent beam. The calculated DCSs show pronounced diffraction oscillations in this strongly forward scattered region, but the angular resolution of the experiments would be insufficient to resolve these structures clearly, even with greater initial state purity. The angular resolution is limited by the velocity and angular spreads of the two molecular beams, and for the current experiments on the CD$_3$ + D$_2$/H$_2$ systems, varies from 3° to 18° depending on the scattering angle.

The error bars associated with the experimental DCSs were determined by combining the standard deviation determined from comparison of several measured images for a single final state with the uncertainty introduced by application of the density-to-flux transformation. The latter factor was quantified by comparing DCSs extracted from the two halves of the image separated by the relative velocity vector (which should be symmetric after perfect transformation).

There is generally quantitative agreement between the (normalized) experimental and computed DCSs, although some small discrepancies are evident for scattering angles <45° for some probe transitions with $n' \leq 4$. Here, the experimental DCSs are slightly larger than the computed DCSs, which could be a consequence of our limited experimental angular resolution or imperfect background subtraction. There may also be contributions to the scattering signals from initial levels with higher initial $n$ present at low density in our ~15 K beam, because elastic scattering events will give strong forward scattering with high integral cross sections. The only significant differences between the experimental and computed DCSs are for detection of some high-$n'$ final rotational levels, in particular via the $S(5)$ and $S(6)$ lines in collisions with D$_2$ and the $R(5)$ and $S(5)$ lines in collisions with H$_2$. Even for these cases, there is satisfactory qualitative agreement between the shapes of the experimental and computed DCSs.

IV. DISCUSSION

Although the focus of our study is on inelastic scattering, the collision of a methyl radical with molecular hydrogen can also follow a reactive pathway. However, the
vibrationally adiabatic barrier height on the potential energy surface for reactive formation of methane and atomic hydrogen has been computed to be 3847 cm$^{-1}$. This energy barrier is much higher than the collision energy in our experiments and calculations so the reactive path is closed. Moreover, the PES was computed with the assumption of rigid molecular geometries. Our comparisons of experimental and computed DCSs therefore test the quality of the \textit{ab initio} PES and the accuracy of the scattering calculation methods in regions of the global PES below the transition state for reaction.

For both D$_2$ and H$_2$ as collision partners, the measured images and the corresponding DCSs directly reveal the dependence of the scattering upon CD$_3$ final rotational angular momentum $n'$. The DCSs peak in the forward hemisphere for $n' = 2$–4 and shift more to sideways and backward scattering for $n' = 5$. For $n' = 6$–8, the DCSs are dominated by backward scattering. A similar trend was observed for scattering of methyl radicals with He, and we discussed the origins of this behavior in terms of partial cross sections (or impact-parameter dependence of the scattering) in a recent paper. DCSs were measured for different spectroscopic branches to probe a given methyl rotational level $n'$, but a different subset of the $k'$ projection quantum numbers. These DCSs differ, especially for $n' = 5$, demonstrating the sensitivity of scattering to the $k'$ value, even if it is not fully resolved in the current experiments.

With inspection of Figs. 7–10, we see that there are a few clear differences between DCSs measured for H$_2$ and D$_2$ as collision partners with CD$_3$, the most apparent being that the DCSs for the CD$_3$–D$_2$ system decrease more sharply from a maximum at small scattering angles towards larger angles. In view of good agreement between the experimental and computed DCSs, we can compare in detail the computed state-resolved DCSs for the two systems. It should be noted that we have no clear experimental information on the rotational inelasticity of the D$_2$/H$_2$ collision partner.

Figure 11 compares the DCSs for transitions from the CD$_3$ 1$_0$ rotational level, the lowest level of $A_1$ nuclear spin modification, into selected final levels in collisions with D$_2$ and H$_2$ at relative translational energies of 640 and 680 cm$^{-1}$, respectively. State-to-state ICSs corresponding to the DCSs plotted in Fig. 11 are displayed in Fig. 4 for D$_2$ as a collision partner. DCSs for transitions involving other final levels and for collisions out of the 0$_1$ and 1$_1$ rotational levels, the lowest levels of the $A_2$ and $E$ nuclear spin modifications, respectively, can be found in the supplementary material. We see in Fig. 11 that DCSs for the same transitions have a similar angular dependence for the D$_2$ and H$_2$ collision partners. For final levels $n' \leq 4$, the DCSs for the D$_2$ collision partner are larger for small angles, while the DCSs for H$_2$ extend to larger scattering angles than do the DCSs for D$_2$. For intermediate states ($n' = 5$ and 6), the DCSs for D$_2$ are dominated by sideways scattering with peaks around $\theta \sim 90^\circ$, whereas the DCSs for...
H₂ are shifted more to backward hemisphere. The DCSs for higher final levels are dominated by backward scattering for both collision partners as demonstrated in Fig. 11 by DCSs for the \( \gamma_0 \) final level. We notice that the CD₃–D₂ DCSs are very similar for the D₂ \( j_2 = 0 \) and 1 initial rotational levels. The DCSs for the \( j_2 = 0 \rightarrow 2 \) transition (not plotted) are in general more backward scattered for H₂ than for D₂ for small \( \Delta n \) changes (\( n' \leq 5 \)) and have the same angular dependence for larger \( \Delta n \) changes. In addition, for a given CD₃ transition, the ratio of the ICSs for the \( j_2 = 0 \rightarrow 2 \) to the \( j_2 = 0 \rightarrow 0 \) transition is much smaller for the H₂ collision partner than for D₂; this is presumably due to the larger energy gap for \( \Delta j_2 = 2 \) transition in H₂. The PESs for CD₃–D₂ and CD₃–H₂ scattering are identical, so observed differences in DCSs must be attributed to the effects of different masses of the collider, and any associated changes to the quantized rotational energy levels of H₂ and D₂.

Conversely, collisions of CD₃ with D₂ and He have the same reduced mass, but are governed by different PESs. A further difference between He and D₂ collision partners is that D₂ has a rotational degree of freedom, so can be rotationally excited or de-excited in a collision, and collisions can also occur with an initially rotationally excited molecule. In our experiments (present work and Ref. 36), the D₂ molecular beam has a larger mean speed than does the He beam (because of the larger heat capacity ratio for a monatomic gas (\( \gamma = 5/3 \)) than for a diatomic gas (\( \gamma = 7/5 \))). To make a clear comparison of these two systems, we have calculated CD₃–He DCSs at the same collision energy (and hence relative velocity) as the present experiments on CD₃–D₂. Figure 12 presents computed DCSs for selected transitions from the \( \gamma_1 \) rotational level, the lowest level of the \( E \) nuclear spin modification, for CD₃ in collisions with D₂ and He at a collision energy of 640 cm⁻¹. Each DCS depicted represents an example of a transition directly coupled by one of the largest expansion coefficients of the PES for the CD₃–He system (see Fig. 3 in Ref. 45). For the D₂ collision partner, DCSs are presented for initial rotational levels \( j_2 = 0 \) and 1, with no collision-induced change in \( j_2 \). DCSs for a wider range of CD₃ initial and final rotational levels can be found in the supplementary material. The DCSs for initial \( j_2 = 1 \) of D₂ are often larger, in particular in the forward direction (note the scaling of the \( j_2 = 1 \rightarrow 1 \) DCS in Fig. 12(a)).

The CD₃–D₂ DCSs show similar propensities for changes in the CD₃ rotational quantum numbers \( n \) and \( k \) as for CD₃–He collisions. For small changes \( \Delta n \) in the rotational angular momentum, the DCSs for \( \Delta k = 0 \) transitions have fairly sharp forward peaks and broad, lower intensity peaks in the backward hemisphere (Fig. 12(a)). These transitions are enabled mainly by the \((l_1, \mu_1) = (2, 0)\) terms, in a similar fashion to the role of the \( v_{33} \) term for CD₃–He. The \( \Delta k \neq 0 \) transitions for small \( \Delta n \) changes display broad DCSs extending over the entire angular range, with oscillations for angles \( \gamma \leq 45° \) (Fig. 12(b)). Such transitions involve direct coupling through the \((l_1, \mu_1) = (3, 3)\) terms, in analogy to the role of the \( v_{33} \) term for CD₃–He. The \( \Delta k = 1 \) transitions for the \( E \) nuclear spin modification, e.g., the \( l_1 \rightarrow 33 \) transition in panel (b), have DCSs very similar in shape to those for \( \Delta k = 3 \) transitions for \( A_1 \) and \( A_2 \) levels, e.g., the \( 0_0 \rightarrow 33 \) transition. As discussed in detail previously for CD₃–He, \( \Delta k \neq 0 \) transitions for \( E \) levels are also enabled by the \((l_1, \mu_1) = (3, 3)\) terms. For transitions with larger changes in the rotational quantum number \( n \), the DCSs shift toward the backward hemisphere, as can be seen in the comparison of experimental and computed DCSs displayed in Figs. 8 and 10 for D₂ and H₂ collision partners, respectively.

V. CONCLUSIONS

The experimental measurements reported here of inelastic scattering of CD₃ radicals with H₂ and D₂ molecules represent the first DCSs obtained for collisions of a polyatomic radical with a diatomic molecule. We have compared these experimental DCSs with the outcomes of close coupling quantum-mechanical calculations performed using a newly determined \textit{ab initio} PES computed at the RCCSD(T)-F12a level of theory. We find good agreement between the experimental and calculated DCSs, with the exception of scattering into the \( n' = 5 \) and 6 levels of CD₃, as probed by the \( S(5) \) and \( S(6) \) REMPI lines in collisions with D₂ and the \( R(5) \) and \( S(5) \) lines in collisions with H₂. This agreement suggests that the PES and the scattering calculations provide an accurate description of the interaction of CD₃ with these diatomic molecules, at least at energies around 600–700 cm⁻¹ corresponding to our experimental conditions.

The DCSs for inelastic scattering of CD₃ with H₂ and D₂ peak in the forward hemisphere for \( n' = 2–4 \) and shift more to sideways and backward scattering for \( n' = 5 \). As the energy
transfer in a collision increases, the DCSs are increasingly dominated by backward scattering (n′ = 6–8). This same behavior is recognized for inelastic scattering of diatomic and polyatomic molecules and it is also consistent with our prior report36 of inelastic scattering of CD3 with He. DCSs for a given n, k → n′, k′ transition show similar angular dependences for D2 and H2 as collision partners. Since CD3–D2 and CD3–H2 interactions are described by the same PES, small differences between DCSs or ICSs for D2 and H2 collision partners can be attributed to mass effects, or, in the case of transitions involving a change in the rotational angular momentum of the diatomic collider, to mass-related changes in the quantized energy level structure.

We also computed rotational-level resolved integral cross sections for collision of CD3 with D2 and H2. The ICSs for inelastic scattering of CD3 with D2 and H2 j2 = 1 are larger than for j2 = 0, indicating that an initially rotating D2 or H2 molecule increases the probability of a given CD3 transition. The ratio of ICSs for j2 = 0 → 2 to j2 = 0 → 0 transitions in the diatomic, for a particular change in the CD3 angular momentum, is much smaller for H2 than for D2 because of the larger energy gap between rotational levels of the lighter isotopologue. CD3–D2 DCSs are very similar for collisions with D2 initially in j2 = 0 and 1 rotational levels.

We also compare the DCSs for CD3–D2 with CD3–He measured previously.36 Comparison of these systems is interesting because they have the same reduced mass, but the scattering dynamics of CD3 with D2 and He are governed by different PESs, and thus the forces acting between the collision partners. For example, the global minimum of the CD3–D2 PES has Dc = 99.0 cm−1, which is significantly larger than for CD3–He [27.0 cm−1 (Ref. 37)]. The equilibrium geometry for CD3–D2 is R = 6.57 bohr, θ1 = 0°, θ2 = 0°. The D2 molecule thus lies along the C3 axis of the methyl radical as opposed to the equilibrium geometry of the global minimum for CD3–He, for which the He atom lies in the molecular plane and bisects two C–H bonds at R = 6.52 bohr.

When comparisons are made between computed DCSs for CD3–D2 and CD3–He scattering at the same collision energy, we find a similar dependence on scattering angle. This observation is particularly the case for transitions directly coupled by terms representing the threefold anisotropy associated with the azimuthal angle about the C3 symmetry axis of the radical. ICSs for CD3–He and CD3–D2, in which the D2 is in an initial level with j2 = 0, are of comparable magnitudes.

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