

COLLISIONAL INTERFERENCE
IN THE INFRARED SPECTRUM OF HD:
CALCULATION OF THE LINE SHAPE
OF VIBROROTATIONAL TRANSITIONS FOR HD-He

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ABSTRACT

The line shape parameters for the collision-induced vibration-rotation spectrum of HD-He are calculated with the formalism of Gao et al. The total intensity interference parameters and line asymmetry parameters are found to be larger than those for pure rotational transitions. The results depend on collisional propagation among rotational levels in both vibrational states and can be sensitive to vibrational-state dependence of the intermolecular potential.

I. INTRODUCTION

Coherence, which is a necessary ingredient for the occurrence of interference, is a manifestation of indistinguishability. In this paper the amplitudes for two electric-dipole transitions between the same initial and final states are considered and are shown to be capable of interference despite vastly different origins.

One of these is an allowed electric dipole transition which follows the selection rule $\Delta J = \pm 1$. The associated line shape is that typical of an allowed transition sensitive to the intermolecular processes which give rise to the phenomenon of collision-broadening with broadening coefficients 10^{-3} – 10^{-2} cm⁻¹/atm in the impact limit. The other transition is a collision- or interaction-induced electric dipole transition for which line shapes are generally very broad (10–100 cm⁻¹) and not sensitive to pressure changes of less than hundreds of atmospheres.

Collision-induced transitions occur quite generally and are due to dipoles induced in pairs or higher order clusters of molecules through molecular interactions. The symmetric molecule H₂ does not have a permanent dipole moment nor an allowed infrared spectrum, but it does show a collision-induced spectrum which has been extensively studied [1].

The particular molecule considered here is the hydrogen isotopomer HD which has a small permanent dipole moment of the order 10^{-4} – 10^{-3} D lying along the internuclear axis. As a result HD has an allowed infrared spectrum. The small size of the moment moreover

makes HD an almost unique case for the study of interference between allowed and induced transitions. Usually such interference effects are masked by strongly allowed transitions. Elucidation of the effect promises to lead to increased understanding of the anisotropic interaction between diatomic molecules in dense media. The phenomenon was discovered in vibration-rotation spectra by McKellar [2] and the pioneering theoretical explanation given by Herman, Tipping and Poll [3-6].

Since HD is a heteronuclear molecule, its centres of mass and charge do not coincide. This circumstance results in components of the induced dipole moment which permit transitions $\Delta J = \pm 1, \pm 3, \dots$ in addition to the $\Delta J = 0, \pm 2$ leading terms for H_2-H_2 pairs. If interference is to occur both the allowed and induced dipole moments must be of the same symmetry, that is, give rise to the same selection rules. The induced dipole moment in HD-X, where X is a perturber, can contain a component of the required symmetry, usually labelled $A_1(100)$ [4], which does not depend on the orientation of the perturber or of the intermolecular axis. This component lies in the direction of the internuclear axis of HD, either parallel or antiparallel to the allowed moment, thereby leading to constructive or destructive interference. The induced moment dies away quickly, as it depends strongly on the magnitude of the intermolecular distance. Another collision can induce another dipole with a component in the same direction. The allowed dipole transition is perturbed by collisions and undergoes collision-broadening. The phase associated with the induced transition is locked to that of the allowed transition with a loss of phase correlation in time for both caused by collision-broadening type encounters [7]. The resulting line shape is a narrow feature, with a width characteristic of collision-broadening, rather than a broad profile which accompanies pure collision-induced transitions.

Experimentally in dense gases, unlike an ordinary allowed transition, the total intensity of an individual narrow line is found to be a function of perturber density, increasing or decreasing as the density increases [8]. The profile is nearly Lorentzian at low density but an asymmetry develops as the line broadens with increasing density [2]. For vibration-rotation transitions this asymmetry is extremely pronounced at high density (150 amagats).

II. THEORY

Gao, Tabisz, Trippenbach and Cooper have developed a general theoretical description of the phenomenon [9]. It is this treatment which forms the basis of the calculations reported in the present paper.

The system considered is a single neutral radiator (absorber) contained in a gas of N molecules and immersed in a radiation field. The radiator (or absorber) has a series of low lying closely spaced energy levels (associated with vibration-rotation levels of HD). The perturbers have widely spread levels (to be associated with electronic levels of inert gas atoms). Electric dipole allowed transitions are assumed possible between levels of both the radiator and the perturber. In addition, interactions between the radiator and perturber will induce cluster dipole moments which also act in radiative transitions occurring at the same frequencies as the allowed transitions. Absorption and stimulated emission events are considered. The lifetimes of the excited states are long compared to the duration of a collision τ_c and the time between collisions. Therefore spontaneous emission is ignored. The spacing of the radiator states is not large compared to \hbar/τ_c or to kT . Therefore radiator-

perturber interactions can cause inelastic collisions and transitions among radiator states. The essential elements of the problem are: transitions due to allowed and induced moments, possibility of interference between them, effects due to single and successive collisions. The use of an anisotropic intermolecular potential allows components of the induced dipole moment other than just $A_1(100)$ to participate in the interference effect [4].

The final expressions obtained for the absorption coefficient $\alpha(\omega)$ at frequency ω is [10]:

$$\begin{aligned} \alpha(\omega) = n_R \left(\frac{4\pi^2 \omega}{3\hbar c} \right) (1 - e^{-\beta\hbar\omega}) P(J_g) |\mu_R|^2 \\ \times \left(\frac{Bn_p/\pi}{(\Delta - Sn_p)^2 + (Bn_p)^2} (1 + an_p + bn_p^2) \right. \\ \left. - \frac{(\Delta - Sn_p)/\pi}{(\Delta - Sn_p)^2 + (Bn_p)^2} (cn_p + dn_p^2) \right). \end{aligned} \quad (1)$$

with

$$\gamma = n_p \left[1 - \sum_{\substack{m_e, q, m_g \\ m_e, m_g}} (-1)^{m_e + m_g} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix} \langle J_e m_e' | \hat{S} | J_e m_e \rangle \langle J_g m_g' | \hat{S} | J_g m_g \rangle^* \right]_{coll} \quad (2)$$

$$= n_p (B + iS), \quad (3)$$

$$\mu_1 = \sum_{J_i} \mu_{2p}(J_i) = y_1' + iy_1'', \quad (4)$$

$$\mu_2 = \sum_{J_i} \mu_{2p}(J_i) e^{-\beta(E_i - E_g)} = y_2' + iy_2'', \quad (5)$$

and

$$\mu_{2p}(J_i) = \sum_{m_e q, m_g, m_i} (-1)^{J_e - m_e} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix} \times \int_{-\infty}^{\infty} dt_0 e^{-i\omega_e t_0} [\langle J_e m_e | U^I(\infty, t_0) [\hat{\mu}_e^I(t_0)]_q U^I(t_0, -\infty) | J_i m_i \rangle \langle J_g m_g | \hat{S} | J_i m_i \rangle^*]_{coll}. \quad (6)$$

Then,

$$a = (y_1' + y_2')/\mu_R, \quad (7)$$

$$b = (y_1' y_2' - y_1'' y_2'')/\mu_R^2, \quad (8)$$

$$c = (y_1'' + y_2'')/\mu_R, \quad (9)$$

$$d = (y_1' y_2'' + y_1'' y_2')/\mu_R^2. \quad (10)$$

Here n_R and n_p are the radiator and perturber number densities; β is $1/k_B T$; $P(J_g)$ is the Boltzmann distribution function for the initial state J_g ; μ_R is the reduced matrix element for the allowed radiator dipole $\langle J_e \| \mu_R \| J_g \rangle$, where J_e refers to the final state. The parameters B and S are the line broadening and frequency shift coefficients in the impact approximation. The detuning $(\omega - \omega_{eg})$ is given by Δ . The total line shape is the sum of Lorentzian and dispersion components whose relative strengths are given, respectively, by the quantities a and b and c and d . They in turn depend on matrix elements μ_1 and μ_2 of the induced dipole moment μ_e divided by the allowed moment or allowed moment squared. The superscript I denotes the interaction picture and the U^I is the time evolution operator. The subscript $coll$ denotes an average over classical trajectory quantities, namely impact parameter and velocity.

This formalism has been applied in the calculation of the spectral parameters for pure rotational transitions in HD-He and HD-Ar [10]. The major conclusion of that work is that collision propagation among rotational states play an important role in the determination of these line shape and interference parameters. Thus, for example, for the interference term associated with a transition occurring between J_g and a final state J_e , the molecule may enter a collision at $t = -\infty$ in some arbitrary state. The system propagates to $t = t_0$ while the absorber may possibly undergo J - and/or m -mixing. At $t = t_0$ the induced dipole operator acts, in general, between two intermediate states J_x and J_y of the absorber. The system then propagates to the end of the collision at $t = +\infty$ with the absorber again possibly experiencing

J - and/or m -mixing. At $t = +\infty$, there remains coherence between $|Jm\rangle$ and $|J_g m_g\rangle$. The allowed dipole interacts with the light field at some later time to leave the molecule in J_e .

This m - and particularly J -mixing (inelastic collisions) have a profound effect on the calculated parameters. The relative strength of various mixing processes is controlled by a factor of the form $\exp(\pm i(\omega_{eg} - \omega_{xy})\tau_c)$ where $\omega_{eg} - \omega_{xy}$ is the frequency difference between the transitions $g \rightarrow e$ and of $x \rightarrow y$; J -mixing is important if $(\omega_{eg} - \omega_{xy})\tau_c \leq 1$. Calculations are reported for HD-He and HD-Ar in reference 10.

The purpose of the present paper is to extend these calculations to the vibration-rotation spectrum. In this case collisional propagation can occur in principle among levels in the ground vibrational state, among levels in the excited vibrational states and between levels in the two vibrational states. The collision duration is too long and the temperature too low to make this last contribution significant. It is neglected in the following analysis.

III. CALCULATION

In order to perform the calculation three quantities are needed: allowed dipole transition elements, the induced dipole transition elements and the intermolecular potential.

Allowed dipole elements have been calculated by Wolniewicz [11]. They are approximately $-8.3 \times 10^{-4} \text{D}$ for pure rotation transitions ($R_0(J)$ lines) and have the following values for particular vibration-rotation transitions from the $v = 0$ to $v = 1$ state ($P_1(J)$, $R_1(J)$ lines): $P_1(1)$, $+4.85 \times 10^{-5} \text{D}$; $R_1(0)$, $+5.60 \times 10^{-5} \text{D}$; and $R_1(1)$, $+5.9 \times 10^{-5} \text{D}$; J refers to the initial rotational state. Ab initio calculations of the induced dipole moment involved in the $v = 0$ to $v = 1$ transition for HD-He have been made by Borysow et al [12].

To alter the formalism from that used for pure rotational transitions the following are necessary. The rotational energy level constants depend on vibrational state; for example $B_0 = 44.6665 \text{ cm}^{-1}$ and $B_1 = 42.7383 \text{ cm}^{-1}$ where B_v is the rigid rotor rotational constant giving the energy $E_J = B_v(J)(J+1)$. Such differences affect the degree of mixing within the rotational manifolds in the ground and excited vibrational states, as the frequencies ω_{eg} and ω_{xy} depend on B_v . The vibrational dependence of the wave function is included in calculation of the induced dipole element which does not depend explicitly on the internuclear distance. The calculation reduces to elements which depend only on rotational wavefunctions. These are taken to be spherical harmonic functions, identical in the $v = 0$ and $v = 1$ states. The selection rule now is $\Delta J = \pm 1$ as contrasted with the $\Delta J = +1$ for pure rotation states.

The intermolecular potential is in general dependent upon vibrational state. The calculations have been performed in two ways: (i) with the same potential when the molecule is in the initial and final vibrational states and (ii) with a simply modelled vibrational state dependent potential. The first case assumes the HD molecule is a rigid rotor, while the second is an attempt to include HD vibrations in the model.

Vibrational dependence was introduced into the potential, in an admittedly crude manner, by following the method of Stefanov [13] making the potential sensitive to the collisional diameter in each vibrational state. The rotational constant B_v is inversely proportional to the internuclear distance r_v . If a head-on collision is assumed, the collisional diameters σ_1 and σ_0 for the two vibrational states are related by $\sigma_1 - \sigma_0 = (r_0/2)(\Delta - 1)$ where Δ is the ratio $(B_0/B_1)^{1/2}$. The potential used is that for H_2 -He developed by Mulder et al [14]. The isotropic part of this potential is shifted to produce a zero at σ_1 but remain unchanged at

large R . The resultant potentials have the following parameters: $\sigma_0 = 3.0382 \text{ \AA}$, $R_0^{\min} = 3.420 \text{ \AA}$ and $\epsilon_0 = 12.919 \text{ K}$ and $\sigma_1 = 3.0466 \text{ \AA}$, $R_0^{\min} = 3.428 \text{ \AA}$ and $\epsilon_1 = 12.748 \text{ K}$.

The origin of this potential is shifted from the centre of mass of H_2 to the centre of mass of HD [4,10]. This shift gives a vibrational state dependence to both the isotropic and anisotropic components of the resulting HD-He potential. In principle, the isotropic part of the HD-He potential should be employed in the calculations of the collision trajectory. Because of the convenience of the analytical expression for the H_2 -He potential, its isotropic part was in fact used. This approximation does not introduce a significant error into the calculation.

When the potential is made dependent on vibrational state, several additional changes in the computational procedure ensue. When the collision partners enter the collision, the molecule HD is in the ground vibrational state and the intermolecular potential is denoted $V(v=0)$. After the induced dipole moment operator has acted, the molecule is in the excited state the potential is $V(v=1)$. This situation affects the nature of the collisional propagation, calculated through matrix elements of the time evolution operator and the S-matrix (see eqns. (2) and (6)).

The trajectory for a particular collision should also be modified, as the potential will have changed once the induced dipole has acted. The change, however, is small, less than the error introduced by using the H_2 -He potential to calculate trajectories. The potential $V(v=0)$ is therefore used to calculate the trajectories.

These changes have been incorporated into the codes used for the pure rotational transitions and calculations made for 77, 195 and 295 K. The results are given in Table 1, together with those for pure rotational transitions and experimental data, where available.

IV. DISCUSSION

As shown in eqns. (7) - (10), the parameters a and c depend on $(\mu_R)^{-1}$ and b and d on $(\mu_R)^{-2}$. Recall that μ_R is about -8.3×10^{-4} for the pure rotational transitions and $+5.5 \times 10^{-5}$ for the lines of the fundamental band. By this reckoning, a and c should differ by about a factor of ~ 15 between the two types of transitions; similarly both b and d should differ by about 230 between these cases. In fact, a and c are always of opposite sign and have larger magnitude for the vibrational case; b and d usually have the same sign and again are larger for the vibrational lines. Their ratios for corresponding $R(J)$ transitions can however be considerably different from 15 and 230; collisional propagation in the excited vibrational state is thereby shown to be important.

Comparison with experiment is possible only for $R_J(0)$ and $R_J(1)$ at 77 K. Agreement for a is quite good and reasonable for b , parameters affecting the total intensity in the line. The calculated asymmetry parameters c and d are, on the other hand, too small, especially for $R_J(1)$. The calculation does predict a large asymmetry, but not as large as experiment shows.

When an intermolecular potential independent of vibrational state is used in the calculation, the parameters do change, all of them decreasing: a by less than 1%, b by up to 5%, c by 2 to 25%, and d by 2 to 15%. The largest changes occur at 295 K. The broadening coefficient B changes uniformly by about 1-2%.

Previous work [10] has shown that collisional propagation is important to the description of collisional interference, particularly to the line asymmetry. Investigations of the

contributions of individual components of the induced dipole moment revealed that different components play major roles in the intensity interference and line asymmetry phenomena [17]. The present results indicate that the intensity effect is not very sensitive to the vibrational state dependence of the intermolecular potential but that the line asymmetry is. Collisional interference seems to consist of two distinct effects which may be complementary sources of information on intermolecular interactions.

Several trends which can be tested experimentally are evident in the calculations:

- (i) The magnitude of the major interference parameter, lal , increases as T increases for a given J , with the greater increase for greater J and for the fundamental band. Also lal increases as J increases at constant T , with the rate of increase greater again for the lines of the fundamental band.
- (ii) The intensity parameter b which describes effects due to induced transitions in successive collisions increases with J at constant T but can increase or decrease as T increases for a given J .
- (iii) The behaviour of c is such that the lines become more asymmetric as T increases at a given J and more symmetric as J increases at constant T .
- (iv) As T increases, d becomes more negative and the effect of this trend can either increase the asymmetry ($R_d(J)$) or decrease the asymmetry ($R_r(J)$). As J increases at constant T , d becomes more positive for $R(J)$ approaching zero and the density squared asymmetry term becomes less important.
- (v) Parameters c and d are usually of opposite sign for the fundamental transitions and thus have opposing effects on the line asymmetry.
- (vi) The asymmetries of $P_r(1)$ and $R_r(0)$ are in opposite directions.

V. CONCLUSION

The interference parameters for several fundamental band vibration-rotation lines in the HD-He spectrum have been calculated at three widely spaced temperatures. Collisional propagation effects are shown to be important among rotational levels in the ground and excited vibrational states. The results are consistent with experimental measurements, particularly the larger interference effects for the vibrational-rotational lines. Detailed agreement with experiment is not achieved. The results can be sensitive to vibrational state dependence of the intermolecular potential.

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Table 1. Spectral Line Shape Parameters: HD-He

| Ref. | a (10^{-2} amagat $^{-1}$) | b (10^{-4} amagat $^{-2}$) | c (10^{-3} amagat $^{-1}$) | d (10^{-5} amagat $^{-2}$) | $B(\text{HWHM})$ (10^{-2} cm $^{-1}$ amagat $^{-1}$) |
|------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|---|
| T = 77 K | | | | | |
| | | | calculation | | |
| present | $P_r(I)$ | -2.09 | 1.22 | -20.0 | 23. |
| | | | | | 0.32 |
| present | $R_r(0)$ | -1.83 | 0.840 | 5.33 | -5.32 |
| | | | | | 0.32 |
| present | $R_r(I)$ | -2.39 | 1.42 | -1.58 | 1.80 |
| | | | | | 0.20 |
| [10] | $R_o(0)$ | 0.299 | 0.023 | -1.2 | -0.20 |
| | | | | | 0.31 |
| [10] | $R_o(I)$ | 0.426 | 0.045 | 0.054 | -0.012 |
| | | | | | 0.19 |
| experiment | | | | | |
| [15] | $R_r(0)$ | -1.44 (2) | 0.17 | 12. | -8.5 |
| | | | | | 0.28 |
| [15] | $R_r(I)$ | -2.46 (2) | 1.2 | 11. | -14. |
| | | | | | 0.31 |
| [16] | $R_o(0)$ | 0.60(16) | | -3.0 (6) | |
| | | | | | 0.15 |
| [16] | $R_o(I)$ | 0.62(7) | | -2.6 (6) | |
| | | | | | 0.20 |

| Ref. | a (10^{-2} amagat $^{-1}$) | b (10^{-4} amagat $^{-2}$) | c (10^{-3} amagat $^{-1}$) | d (10^{-5} amagat $^{-2}$) | $B(\text{HWHM})$ (10^{-2} cm $^{-1}$ amagat $^{-1}$) |
|-----------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|---|
| T = 195 K | | | | | |
| | | | <u>calculation</u> | | |
| present | $P_r(1)$ | -2.19 | 1.22 | -5.80 | 8.58 |
| | | | | | 0.949 |
| present | $R_r(0)$ | -1.88 | 0.857 | 7.07 | -8.36 |
| | | | | | 0.949 |
| present | $R_r(1)$ | -2.68 | 1.81 | 4.22 | -5.85 |
| | | | | | 0.736 |
| [10] | $R_o(0)$ | 0.297 | 0.023 | -1.5 | -0.33 |
| | | | | | 0.93 |
| [10] | $R_o(1)$ | 0.483 | 0.060 | -1.3 | -0.33 |
| | | | | | 0.71 |
| T = 295 K | | | | | |
| | | | <u>calculation</u> | | |
| present | $P_r(1)$ | -2.20 | 1.13 | -2.49 | 4.91 |
| | | | | | 1.47 |
| present | $R_r(0)$ | -1.84 | 0.781 | 7.17 | -9.27 |
| | | | | | 1.47 |
| present | $R_r(1)$ | -2.74 | 1.89 | 6.28 | -9.43 |
| | | | | | 1.22 |
| [10] | $R_o(0)$ | 0.282 | 0.018 | -1.5 | -0.38 |
| | | | | | 1.4 |
| [10] | $R_o(1)$ | 0.491 | 0.063 | -1.9 | -0.51 |
| | | | | | 1.2 |

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