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Collision-induced absorption in the ν_2 fundamental band of $^{12}CH_4$*

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The integrated intensities of the collision-induced absorption of the ν_2 band of $^{12}CH_4$ perturbed by Ar have been calculated theoretically using the *ab initio* calculations, and the value of the quadrupole transition moment we obtained is $\langle 0|Q|\nu_2\rangle = 5.226ea_0^2$. The corresponding experimental value obtained from $^{12}CH_4$–Ar spectra is $|\langle 0|Q|\nu_2\rangle| = 4.931ea_0^2$. Ignoring vibration–rotation interaction and Coriolis interaction, and considering both the theoretical approximations and experimental uncertainties, the agreement can be regarded as good, thus confirming that the enhancement is due to the quadrupole collision-induced mechanism.

Keywords: collision-induced absorption, ν_2 fundamental band, quadrupole transition moment
PACC: 3120A, 3220F, 3370C, 3410

1. Introduction

Collision-induced absorption (CIA) in gaseous methane and its isotopes is a subject of some astronomical interest, particularly since the atmosphere of Titan, a satellite of Saturn, is known to consist of these gases. Methane and its isotopes is an important and relatively abundant constituent of planetary atmospheres. In the last few decades, laboratory studies have found some important phenomena, many of them agree well with theory, but there are still many phenomena for which we have not found their origins. The infrared absorption by $^{12}CH_4$ is important in many applications, particularly in national defence systems, consequently, there are a large number of studies on the various infrared and Raman bands of methane-perturber mixtures.[1] Many studies have been carried out for low densities, however, for higher densities, there are additional absorptions. This enhancement is due to transient dipoles induced during collisions and is generally referred to as CIA.[2] To explain the experimental findings, several different hypotheses have been proposed;[3−5] we suppose the existence of the mechanism of the vibrating quadrupole of $^{12}CH_4$ interacting with the polarizability of the perturber. This mechanism would be present for the absorption in the ν_2 region, even in the absence of Coriolis interaction; that is, there is a nonvanishing quadrupole transition matrix element between the ground and ν_2 vibrational states.

In this paper, we will restrict ourselves to spherical top molecules of $^{12}CH_4$–Ar. By equating the slope of the experimentally determined integrated intensity in the spectral range 1410–2000 cm^{-1} versus the density ρ_{Ar} to the theoretical result, we can obtain a value for the magnitude of the $\langle 0|Q|\nu_2\rangle$ transition moment, which is the only unknown quantity. This transition moment would be very difficult to obtain experimentally because the absorption is very weak. To the best of our knowledge, no *ab initio* value of $\langle 0|Q|\nu_2\rangle$ has been published heretofore, so we have carried out extensive calculations for comparison with the experimental results firstly. The positions and intensities of ν_2 fundamental band of $^{12}CH_4$ are measured with high precision using the Fourier transform spectrometer located at the Mc Math telescope, Kitt Peak National Observatory, Arizona and are successfully modelled.[6]

2. Summary of the theory model

2.1. The experimental value of the quadrupole transition element

The theory of the integrated absorption coefficient is expressed as[7]

$$1/\rho_{Ar}\rho_{CH_4}\int_{1410}^{2000}\alpha(\omega)\mathrm{d}\omega$$

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$$= (4\pi^2/3)\alpha_{\rm F} n_0^2 a_0^5 \sum_{c,J,J'} \omega_{0,J,\nu_2,J'} \times P_J C(J\lambda J';00)^2 B_{\rm C}(R)^2, \quad (1)$$

where $\rho_{\rm Ar}$ and $\rho_{\rm CH_4}$ are the densities in amagat (which is the density at the given temperature and pressure divided by the density at normal temperature and pressure), $\alpha(\omega)$ is the absorption coefficient, $\alpha_{\rm F}$ is the fine structure constant, n_0 is the number density at standard temperature and pressure, a_0 is the Bohr radius, $\omega_{0,J,\nu_2,J'}$ are the methane vibration–rotation frequencies, $C(J\lambda J';00)$ is a Clebsch–Gordan coefficient, $c \equiv \upsilon J \upsilon' J' \lambda L$. Now we consider only one mechanism and neglect the short-range overlap interaction: the isotropic quadrupole induction at λ=2. The function $B(R)$ is the matrix element of this component[8]

$$B(R) = \sqrt{\lambda+1}\alpha_{\rm Ar}\langle \nu J|Q(r)|\nu_2 J'\rangle/R^{\lambda+2} = \sqrt{3}\alpha_{\rm Ar}\langle 0J|Q(r)|\nu_2 J'\rangle/R^4, \quad (2)$$

$$B(R)^2 = 3\alpha_{\rm Ar}^2\langle 0J|Q(r)|\nu_2 J'\rangle^2 I(6), \quad (3)$$

where $a_{\rm Ar}$ is the polarizability of Ar. $\langle 0J|Q(r)|\nu_2 J'\rangle$ is the quadrupole moment matrix element of $^{12}CH_4$, R is the distance between the atom Ar and the centre of mass of $^{12}CH_4$, all in atomic units. The contribution to the moments due to overlap induction is obtained by subtracting out the quadrupolar part and the corresponding moments. In Eq.(3), $I(6)$ can be written in terms of $x \equiv R/a_0$ as

$$I(6) = 4\pi \int_0^\infty \exp(-V_{\rm iso}(x)/kT) x^{-6} {\rm d}x, \quad (4)$$

P_J in Eq.(1) denotes the Boltzmann factor of the initial rotational state normalized according to $\sum_J P_J = 1$. Strictly speaking, the Boltzmann factor also depends on the initial vibrational state ν but we will be dealing only with cases in which higher vibrational states are not populated

$$P_J = \frac{g_J \exp(-E_{\rm rot}/kT)}{\sum_J g_J \exp(-E_{\rm rot}/kT)}, \quad (5)$$

where g_J are statistical weights. Substituting Eqs.(3) and (4) in Eq.(1), we can write

$$1/\rho_{\rm Ar}\rho_{\rm CH_4} \int \alpha(\omega){\rm d}\omega = 4\pi^2 \alpha_{\rm F} n_0^2 a_0^5 \alpha_{\rm Ar}^2 I(6) \sum_{J,J'} \omega_{0,J,\nu_2,J'} \times P_J C(J2J';00)^2 \langle 0J|Q(r)|\nu_2 J'\rangle^2, \quad (6)$$

where $\Delta J = 0, \pm 2$. Equating this equation to the experimental value 1.350 $\rm cm^{-2}/amagat^2$, we can obtain the only unknown quantity of the absolute magnitude of the quadrupole transition moment, its value being $4.931 e a_0^2$. Considering a small fraction of the allowed intensity of the ν_2 band that lies outside of the range of integration (mostly under the strong ν_4 band), we should regard the experimental value 4.931 $e a_0^2$ as a lower limit.

2.2. *Ab initio* calculations of the quadrupole transition element

The traceless electric quadrupole moment tensor $Q(r)$ with a clamped nuclear geometry can be written as[9,10]

$$Q = \frac{1}{2}\sum_a^N Z_a(3\overline{r_a r_a} - \overline{r_a^2} I) - \frac{1}{2}\sum \langle \psi_0| \sum_i^n (3\overline{r_i r_i} - \overline{r_i^2} I)|\psi_0\rangle, \quad (7)$$

where $\bar{r}_a$ and $\bar{r}_i$ are referred to as vector positions of nuclei and electrons, respectively, Z_a is the atomic number of nucleus a, and I is the unit tensor. The tensor Q depends on the internal degrees of freedom of the nuclei $\{q_1, q_2, \cdots, q_{3N-6}\}$ and thus defines a hypersurface in this $3N-6$ vector space. The vibrational matrix elements are defined as

$$Q_{\upsilon,\upsilon''} = \langle \upsilon''|Q(q_1, q_2, \cdots, q_{3N-6})|\upsilon'\rangle. \quad (8)$$

The calculation of Eq.(8) is usually carried out by expanding Q around the equilibrium geometry in a Taylor series in terms of the vibrational coordinates q_k,

$$Q = Q^{(0)} + \sum_{k=1}^{3N-6} Q^{(1)} q_k + \sum_{k=1}^{3N-6}\sum_{k'=1}^{3N-6} Q^{(k,k')} q_k q_k' + \cdots, \quad (9)$$

where $Q^{(0)}$ is the value of the quadrupole at equilibrium and the quantities $Q^{(k)}, Q^{(k,k')}, \cdots$ are the successive derivatives with respect to $q_k, q_k' \cdots$ calculated at equilibrium. Note that expansion (9) applies to each component $Q_{\alpha\beta}$ ($\alpha, \beta = X$, Y or Z) of the quadrupole tensor. We have calculated, using large-scale *ab initio* methods, the transition moments (8) of methane corresponding to the transition from the ground to the ν_2 vibrational mode. Two matrix elements have been calculated

$$\Theta^{(a)} = \langle 0|Q|\nu_{2a}\rangle, \quad (10)$$

$$\Theta^{(b)} = \langle 0|Q|\nu_{2b}\rangle, \quad (11)$$

where the indices a and b are referred to as the twofold degeneracy of the ν_2 mode which transforms as the E symmetry species of point group T_d. The transition moments (6) and (11) thus reduce to the following one-dimensional expression in the mass-weighted normal coordinate q_{2p},

$$\langle 0|Q|\nu_{2P}\rangle = Q^{(2P)}\langle 0|q_{2p}|\nu_{2p}\rangle = (h/(8\pi^2 c\omega_2))Q^{(2P)}I^{1/2}, \quad (12)$$

where q_{2p} denotes the normal coordinates q_{2a} and q_{2b}, ω_2 is the harmonic frequency of the ν_2 mode. The nonvanishing rule applied to T_d predicts that matrix elements (10) and (11) are nonzero only for the E symmetry components of the quadrupole, namely $(2Q_{ZZ} - Q_{XX} - Q_{YY})$ and $(Q_{XX} - Q_{YY})$.

All calculations are performed using the program Gaussian03 after the geometry has been optimized. The values of the first derivatives $Q^{(2a)}$ and $Q^{(2b)}$ and the corresponding quadrupole transition moments (13) are given in Table 1: The contributions of the nuclei and electrons to the total value of $\Theta^{(a)}_{ZZ}$ are calculated to be 4.8984 and –0.9480 ea_0^2, respectively.

Table 1. First derivatives $Q^{(2a)}$ and $Q^{(2b)}$ of the quadrupole tensor with respect to q_{2a} and q_{2b} (in $ea_0u^{-1/2}$) and the corresponding quadrupole transition moments.

	XX	YY	ZZ		XX	YY	ZZ
$Q^{(2a)}$	–10.0737	–10.0737	20.1474	$Q^{(2b)}$	17.4477	–17.4477	0
$\langle 0\|Q\|\nu_{2a}\rangle$	–1.9752	–1.9752	$\Theta = 3.9504$	$\langle 0\|Q\|\nu_{2b}\rangle$	3.4210	–3.4210	0

Because the contributions from the two degenerate vibrational states add incoherently, the theoretical values for the transition moment is

$$|\langle 0|Q|\nu_2\rangle|_{th} = [\Theta^2 + 3\Theta^2/4]^{1/2} = 5.226ea_0^2. \quad (13)$$

3. Discussion and conclusions

We have made a number of simplified theoretical approximations which are justified by the experimental uncertainties in the measurement of the weak collision- enhancement spectrum; for example, the mechanical and electrical approximations have been assumed in the calculations of Eqs.(10) and (11). This leads to an error of about 1% due to neglecting the nonlinear terms; the J, J' dependence of Q is neglected in Eq.(6) which will contribute much less than 0.5% to the moments. We only include the quadrupolar induction mechanism, in principle, since there should also be overlap terms with octupolar and other symmetries, but we omit these because we expect them to be smaller (a 2%–3% error is produced when we consider octupolar etc); and we aim to give satisfactory predictions that quadrupole moment should dominate the absorptions. In calculating the average over the separation R between the centres of mass, we use only the isotropic part of the interaction potential and assume that the overlap and anisotropy contributions are zero and also neglect the other contributions. In the quadrupolar induction mechanism, we use only the leading long-range part of the induced dipole; as to the Coriolis-allowed dipole-induced dipole (octopole-induced dipole, etc, these will lead to a 2%–3% error), it also makes a very small effect to the total intensity. As the $^{12}CH_4$–$^{12}CH_4$ and Ar–Ar collisions alone are not sufficient to account for the enhancement, we can ignore it. For the far wings of the stronger ν_4 band or the ratio of the components of mixtures, an analysis shows this is also impossible, so we can ignore them too. The simplified theoretical approximations lead to an error of 5%–6% and thus our predictive capability is increased.

The theory presented above is easily generalized to calculate the slope of the enhancement spectra for $^{12}CH_4$–X, X = rare gases and linear molecules, by multiplying the experimental result for $^{12}CH_4$–Ar (1.350) by the ratio $[\alpha_X^2 I(6)_{CH_4-X}/\alpha_{Ar}^2 I(6)_{CH_4-Ar}]$. The major purpose of our work is to generalize the theory to isotopomer collisional pairs, it is successful by comparing with experimental results. We can apply directly the method to more isotopomer collisional pairs. So we can conclude that the observed enhancement of absorption indeed arises from the quadrupolar induction mechanism.

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