

Rovibrational matrix elements of the multipole moments and of the polarizability of the H₂ molecule in the solid phase: Effect of intermolecular potential

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MS received 24 April 2000

Abstract. Rovibrational matrix elements of the multipole moments Q_ℓ up to rank 10 and of the linear polarizability of the H₂ molecule in the condensed phase have been computed taking into account the effect of the intermolecular potential. Comparison with gas phase matrix elements shows that the effect of solid state interactions is marginal.

Keywords. Multipole moments; linear polarizability; solid hydrogen, matrix elements.

PACS Nos 33.15.Kr; 33.70.-w; 34.20.Gj

1. Introduction

The rovibrational matrix elements of the multipole moments and polarizability of molecules find applications in the study of infrared spectra, intermolecular potential and collision-induced absorption phenomena, especially in homonuclear molecules. Because of its simplicity and fundamental importance, the hydrogen molecule plays a central role in molecular physics. Its multipole moments (Q_ℓ) and linear polarizability have been the subject of many theoretical investigations [1–10]. The matrix elements given in the previous works, strictly speaking, have been calculated for the free molecules, but invariably, these gas phase results have been used in the elucidation of absorption features in the characteristic infrared spectrum displayed by H₂ in the condensed state [9–15]. The justification for the adoption of the matrix elements of the free hydrogen molecule to the solid phase will have to rest on rigorous calculations which have not been attempted before. This is the main purpose of the present paper.

Hydrogen is known to form a weak molecular solid [11]. The extreme weakness of the intermolecular forces in crystalline H₂ may be gauged from the fact that the quantized end-over-end rotational levels of the free molecule are preserved in the solid down to 0 K. Consequently, it is natural to expect the matrix elements to undergo but marginal changes as the molecule passes from the free to the crystalline state. In this paper we compute the

rovibrational matrix elements of the multipole moments up to rank 10 and of the linear polarizability of the H₂ molecule in the solid phase and compare the results with that for the free molecule.

The modified Dunham model introduced by Van Kranendonk [11] serves as a convenient starting point to take into account the effect of solid state interactions. As emphasized before, the intermolecular interaction energies are much too small compared to the energy separations between the unperturbed rotation-vibration levels, so much so, the internal rotational and vibrational motions of the molecules in the solid are free in the sense that the vibrational and rotational quantum numbers ν and J remain good quantum numbers. As will be seen at the end of the calculations, the solid phase matrix elements differ up to a maximum of 2% from the free molecule matrix elements.

2. Theoretical details and method of computation

In a linear molecule, the strength of the 2^ℓ -pole moment tensor of rank ℓ is characterized by a single (scalar) component Q_ℓ , and ℓ is necessarily even valued if the molecule is centrosymmetric like H₂. If we align the diatomic molecule along the z -axis and place the origin at the midpoint of the two nuclei, the static multipole moment simply reduces to the sum of two terms, independently representing the contributions from the nuclei and the electrons:

$$Q_\ell(r) = e \left[2Z(r/2)^\ell - \sum_{\text{el}} \langle r_{\text{el}}^\ell P_\ell(\cos \theta) \rangle \right]. \quad (1)$$

Here e is the magnitude of the electronic charge, Z is the atomic number of the nuclei, r is intermolecular distance and r_{el}, θ (the azimuth ϕ being irrelevant) are the polar coordinates of the electron. The summation is over the electrons and the expectation value is over the electronic wavefunctions $\psi(\mathbf{r}_{\text{el}}, r)$ in the adiabatic approximation relevant to the clamped nuclear problem [11]. If we let $\chi_{\nu,J}(r)$ denote the radial part of the rotation-dependent vibrational wavefunction the matrix elements of $Q_\ell(r)$ can be evaluated from

$$\langle \nu J | Q_\ell(r) | \nu' J' \rangle = \int \chi_{\nu,J}(r) Q_\ell(r) \chi_{\nu',J'}(r) dr. \quad (2)$$

The vibrational wavefunction $\chi_{\nu,J}(r)$ for the free molecule can be obtained from the numerical solution of the radial Schrödinger equation for the nuclear motion [11],

$$\left[-\frac{\hbar^2}{2\mu_{\text{nucl}}} \frac{d^2}{dr^2} + U_0(r) + \frac{J(J+1)\hbar^2}{2\mu_{\text{nucl}}r^2} \right] \chi_{\nu,J}(r) = E_{\nu,J} \chi_{\nu,J}(r) \quad (3)$$

in the adiabatic potential $U_0(r)$ using Numerov–Cooley–Cashion method [16]. One can define the matrix elements for polarizability in a way similar to multipole moments where the $Q_\ell(r)$ in eq. (2) is replaced by the isotropic and anisotropic polarizability functions $\alpha(r)$ and $\gamma(r)$, respectively.

Returning now to the solid state effects, the interaction between hydrogen molecules in the solid is discussed in detail in the book by Van Kranendonk [11]. Our estimate of the effect of *intermolecular* potential on the matrix elements is based on the simplified assumption that these interactions change the effective *intramolecular* potentials in the molecules

and the rotation-vibration wavefunctions, but the wavefunctions of the system as a whole remain products of single-molecule wavefunctions. In the analysis of the properties of the solid hydrogen, only the low-lying rotation-vibration states are relevant (indeed we shall restrict ourselves here to $v \leq 3, J \leq 10$) and in considering these states, it is therefore natural to expand the effective potential $U_0(r)$ appearing in eq. (3) around the minimum at $r = r_e$ in powers of the dimensionless (Dunham) variable

$$x = (r - r_e)/r_e. \quad (4)$$

In a free molecule this expansion takes the form

$$U_0(r) = a_0 x^2 (1 + a_1 x + a_2 x^2 + a_3 x^3 + \dots), \quad (5)$$

where a_0 has the dimension of wavenumber and a_1, a_2 , etc. are dimensionless anharmonicity constants characterizing the shape of the potential. Such an expansion is called Dunham expansion.

Van Kranendonk [11] has invoked a model to predict the rovibrational term values in solid hydrogen based on a modification of the Dunham model. In this model the rotation-vibration levels of the H_2 molecule in a solid hydrogen crystal are expressed by a Dunham expansion series, as they can be for the free molecule, employing Dunham coefficients with some additive (dimensionless) correction terms μ_n . Here n accounts for the n th-order contribution of the leading terms of the isotropic intermolecular interaction. This entails a modification of the intramolecular effective potential $U'_0(r)$ in the solid phase as

$$U'_0(r) = U_0(r) + V_1(r), \quad (6)$$

where,

$$V_1(r) = -a_0(\mu_1 x + \mu_2 x^2 + \mu_3 x^3 + \dots). \quad (7)$$

Note that in the definition of $x = (r - r_e)/r_e$, the r_e appropriate for solid state should be used. An estimate of the correction terms μ_n is made recently in ref. [17] by including only the first two parameters μ_1 and μ_2 by fitting the experimentally observed line positions of 15 selected transitions. The resulting best values of these parameters are $\mu_1 = 0.0408$ and $\mu_2 = -0.0179$.

We used the effective intramolecular potential given by eq. (6) in the radial wave equation (3) to calculate the modified rotation-vibration wavefunctions χ'_{vJ} of H_2 in the solid phase. These were subsequently used in eq. (2) to calculate the rovibrational matrix elements of the multipole moments or of the polarizability (where $Q_\ell(r)$ was replaced by the polarizability functions) in condensed phase. In our calculations we used the r -dependent values of $Q_\ell(r)$ reported by Komasa and Thakkar [5] for the 11 bond lengths in the range $0.8a_0 \leq R \leq 2.6a_0$ (a_0 being the Bohr radius) supplemented, whenever possible, by the results reported by Poll and co-workers [2, 3]. The polarizability functions $\alpha(r)$ and $\gamma(r)$ were taken from the work of Rychlewski [6]. The method of computation is similar to what has been described in our earlier works for the free molecule [9,10]. All the calculations were performed using the computer program 'LEVEL 6.0' obtained from Le Roy [18] in which the most accurate adiabatic potential $U_0(r)$ given by Schwartz and Le Roy [19] was incorporated.

Table 1. Comparison of the gas phase and condensed phase adiabatic matrix elements of the \mathcal{Z} -pole moments $Q_\ell (= Q_\ell/ea_0^\ell)$ of H_2 .

ν	J	$\langle 0 J Q_2 \nu J + 2 \rangle^a$		$\langle 0 J Q_4 \nu J + 4 \rangle^a$		$\langle 0 J Q_6 \nu J + 6 \rangle^a$		$\langle 0 J Q_8 \nu J + 8 \rangle^a$		$\langle 0 J Q_{10} \nu J + 10 \rangle^a$	
		Gas ^b	Cond.	Gas ^b	Cond.	Gas ^b	Cond.	Gas ^b	Cond.	Gas ^b	Cond.
0	0	0.484 732	0.485 602	0.340 92	0.342 30	0.226 3	0.227 8	0.155 3	0.156 6	0.114 3	0.115 5
0	1	0.486 855	0.487 728	0.345 55	0.346 96	0.232 1	0.233 6	0.161 3	0.162 7	0.120 3	0.121 6
1	0	0.078 242 5	0.078 330 8	0.118 78	0.119 23	0.114 9	0.115 6	0.099 15	0.099 98	0.085 02	0.085 92
1	1	0.071 963 0	0.072 039 9	0.110 73	0.111 14	0.107 9	0.108 6	0.093 83	0.094 62	0.080 99	0.081 85
2	0	-0.011 635 3	-0.011 668 7	-0.000 607	-0.000 631	0.011 91	0.011 97	0.018 87	0.019 02	0.021 49	0.021 71
2	1	-0.011 818 0	-0.011 850 7	-0.003 116	-0.003 148	0.007 68	0.007 71	0.013 92	0.014 02	0.016 27	0.016 44
3	0	0.001 928 7	0.001 935 5	-0.001 707	-0.001 713	-0.002 83	-0.002 85	-0.002 04	-0.002 07	-0.001 21	-0.001 23
3	1	0.002 129 9	0.002 137 1	-0.001 196	-0.001 199	-0.002 64	-0.002 66	-0.002 40	-0.002 43	-0.002 03	-0.002 07

^aIn atomic units; ^bFrom ref. [9].**Table 2.** Comparison of the gas phase and condensed phase adiabatic matrix elements of the polarizabilities α and γ for H_2 .

ν	J	$\langle 0 J \alpha \nu J \rangle^a$		$\langle 0 J \alpha \nu J + 2 \rangle^a$		$\langle 0 J \gamma \nu J \rangle^a$		$\langle 0 J \gamma \nu J + 2 \rangle^a$	
		Gas	Cond.	Gas	Cond.	Gas	Cond.	Gas	Cond.
0	0	5.417 06	5.424 35	5.430 43	5.437 75	2.029 33	2.035 32	2.040 69	2.046 70
0	1	5.426 68	5.433 99	5.447 78	5.455 12	2.037 17	2.043 18	2.055 66	2.061 71
0	2	5.445 88	5.453 22	5.473 77	5.481 16	2.052 85	2.058 90	2.078 14	2.084 26
1	0	0.739 51	0.740 73	0.634 01	0.635 09	0.611 28	0.612 97	0.572 01	0.573 58
1	1	0.740 56	0.741 78	0.565 15	0.566 15	0.613 03	0.614 72	0.547 38	0.548 88
1	2	0.742 64	0.743 86	0.497 87	0.498 77	0.616 52	0.618 21	0.524 24	0.525 66
2	0	-0.071 035	-0.071 244	-0.069 939	-0.070 151	-0.012 480	-0.012 618	-0.021 245	-0.021 405
2	1	-0.071 264	-0.071 474	-0.067 893	-0.068 106	-0.012 692	-0.012 831	-0.026 636	-0.026 809
2	2	-0.071 725	-0.071 937	-0.064 909	-0.065 121	-0.013 118	-0.013 260	-0.031 719	-0.031 906
3	0	0.009 795	0.009 819	0.010 339	0.010 368	-0.005 632	-0.005 651	-0.003 672	-0.003 684
3	1	0.009 825	0.009 849	0.010 357	0.010 389	-0.005 637	-0.005 656	-0.002 366	-0.002 373
3	2	0.009 887	0.009 911	0.010 104	0.010 138	-0.005 647	-0.005 668	-0.001 066	-0.001 068

^aIn atomic units (a_0^3).

3. Results and discussion

Tables 1 and 2 compare the gas phase and condensed phase rovibrational matrix elements of the multipole moments and polarizability between certain selected states. These are the matrix elements that enter the theoretical absorption coefficients of the various infrared absorption features in solid H_2 . More extensive tabulations of the matrix elements of the multipole moments in gas phase are given in our earlier work [9]; that for the condensed phase can be obtained from the authors on request. Table 3 compares the transition energy of the free molecule with that in the condensed phase for single transitions in solid H_2 that are least affected by the *anisotropic* forces. As may be seen, in the solid the isotropic part of the intermolecular interaction produces shifts in the rotation-vibration levels of the order of 10 cm^{-1} . The results in tables 1 and 2 then show that the effect of this perturbation on the matrix elements is indeed negligible. The natural inference is that the distortion of the rovibrational wavefunction $\chi_{v,J}(R)$ caused by the modified intermolecular potential in the solid is so marginal that it has very little effect on the matrix elements. In general, for Q_2, Q_4 and Q_6 they differ by $< 1\%$ whereas for Q_8 and Q_{10} the difference is $< 2\%$. For some matrix elements like $\langle 0\ 0 | Q_4 | 2\ 4 \rangle$ in table 1 the difference is slightly higher ($\sim 4\%$) mainly due to their intrinsically small magnitudes. Given the accuracy of the absorption coefficient data currently available, the theme of the present paper would suggest that the adoption of the matrix elements of the free H_2 molecule to the solid phase is not a serious source of error. Nevertheless, there is no doubt that in future experiments devoted to the infrared spectroscopy of solid H_2 , more systematic efforts would be lavished on more

Table 3. Comparison of the gas phase (free molecule) and condensed phase transition energy (E) for H_2 for some selected single transitions.

Transition	$E_{\text{gas}}^{\text{a}}$ (cm^{-1})	E_{cond} (cm^{-1})		$E_{\text{gas}} - E_{\text{cond}}$ (Obs.) (cm^{-1})
		Obs. ^b	Cal. ^c	
$U_0(0)$	1168.78	1167.12	1166.21	1.66
$W_0(0)$	2414.76	2410.54	2409.55	4.22
$W_0(1)$	3069.07	3063.48	3062.19	5.59
$Y_0(0)$	4051.73	4044.18	4042.98	7.55
$Q_1(1)$	4155.25	4146.51	4146.77	8.74
$S_1(1)$	4712.91	4704.44	4703.16	8.47
$U_1(0)$	5271.36	5261.28	5260.38	10.08
$U_1(1)$	5695.45	5684.61	5683.48	10.84
$W_1(0)$	6454.28	6441.81	6440.72	12.47
$W_1(1)$	7068.94	7055.37	7054.00	13.57
$Y_1(0)$	8007.77	7991.71	7990.44	16.06
$Q_2(1)$	8075.31	8058.72	8058.71	16.59
$Q_2(0)$	8086.93	8070.44	8070.38	16.49
$U_2(0)$	9139.86	9122.21	9120.87	17.65
$Q_3(0)$	11782.36	11758.73	11758.06	23.63

^aObserved transition energy from ref. [20]. ^bFrom ref. [17]; ^cObtained in the present work during the computation of the adiabatic rovibrational matrix elements in the condensed phase using the effective potential given by eq. (6), with $\mu = 0.0408$ and $\mu_2 = -0.0179$.

precise measurements of the absorption coefficients and when this is done, the labor that has gone into the present calculations (tables 1 and 2) would stand vindicated.

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