

Rovibrational matrix elements of multipole moments of the heavier isotopomers of molecular hydrogen

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Abstract : Rovibrational matrix elements of the multipole moments Q_ℓ of D_2 , T_2 , HD, HT and DT for ranks $2 \leq \ell \leq 11$ have been computed. Since the present calculations have been performed with the nuclear center of mass (rather than the geometric center) as the origin, the computations had to include even as well as odd values of ℓ for the heteronuclear species HD *etc.* unlike for their homonuclear counterparts H_2 , D_2 *etc.* wherein only even ℓ can occur. The results are used to correlate the absorption intensities of the zero-phonon single transitions in solid HD and D_2 to theory.

Keywords : Multipole moments, solid hydrogen, infrared spectra

PACS Nos. : 35.20.My; 33.20.Ea; 78.30.Hv

1. Introduction

Hydrogen, being the simplest of all molecules, holds a rare fascination for the theoretical and experimental investigators alike. The multiple moments (Q_ℓ) of H_2 and its isotopic variants (D_2 , T_2 , HT, *etc.*), among other things, find applications in the interpretation of the 'enforced' infrared spectrum of these molecules peculiar to their condensed phase. Recently, we reported matrix elements of multipole moments of the H_2 molecule up to rank 10 and used them to predict the intensities of the zero-phonon transitions in solid- H_2 [1]. In this paper we extend the calculations to the heavier isotopomers of the hydrogen molecule. The computations of the rovibrational matrix elements of (Q_ℓ) for homonuclear species D_2 and T_2 is straightforward, but for the heteronuclear varieties HD, DT *etc.* the calculations become a much more elaborate exercise due to the non-coincidence of the geometric charge center with the center of mass (CM) of the molecules. Therefore, for the heteronuclear isotopomers it is necessary to first transform all the bond distance-dependent multipole moment functions to the CM coordinates. As a result, the computations had

to include even as well as odd values of ℓ , unlike for their homonuclear counterparts H_2 *etc.* wherein only even ℓ can occur. The details of computations, the results obtained, and illustrative applications will be mentioned in this paper.

2. Method of computation

It is useful to recall that in a linear molecule like D_2 , HD *etc.*, the strength of the multipole moment tensor of rank ℓ is characterized by a single (scalar) component Q_ℓ which depends parametrically on the internuclear separation R . Explicitly,

$$Q_\ell(R) = e \left[2(R/2)^\ell - \left\langle \sum_{\alpha\ell} r^\ell P_\ell(\cos\theta) \right\rangle \right] \quad (1)$$

In order to obtain the rovibrational matrix elements of the multipole moments, essentially, one computes the integral

$$\langle vJ | Q_\ell(R) | v'J' \rangle = \int \chi_{vJ}(R) Q_\ell(R) \chi_{v'J'}(R) dR \quad (2)$$

where, $\chi_{vJ}(R)$ denotes the rotation dependent vibrational wavefunctions defined in the center of mass (CM) reference frame. In our calculations we used the R -dependent values

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of $Q_\ell(R)$ by Komasa and Thakkar [2] for the 11 bond lengths in the range $0.8a_0 \leq R \leq 2.6a_0$ (a_0 being the Bohr radius). For the heteronuclear isotopomers, the center of mass (CM) does not coincide with the center of charge (CC); it is necessary to first transform the multipole moments reported in [2] (which are valid in the CC coordinates of these molecules) to the CM coordinates. Following Gray [3], this transformation can be achieved by the relation :

$$Q_\ell^{\text{CM}}(R) = Q_\ell^{\text{CC}}(R) + \sum_{\ell_1=0}^{\ell-1} \frac{(-1)^{\ell-\ell_1} \ell!}{\ell_1!(\ell-\ell_1)!} \Delta^{\ell-\ell_1} Q_{\ell_1}^{\text{CC}}(R) \quad (3)$$

where Δ is the distance between the two origins. The value of Δ depends parametrically on the internuclear separation R and mass (m) of the two nuclei. It is easy to show that,

$$\Delta = \left(\frac{m_>}{m+m_>} - \frac{1}{2} \right) R \quad (4)$$

It is worth mentioning here that in the CC reference frame, all the odd order multipole moments vanish except for a weak oscillating electric dipole moment (Q_1) which too may be neglected in the first approximation. The rest of the computational method is similar to what has been described in our earlier paper [1]. In brief, the desired smooth $Q_\ell(R)$ function were obtained by 10-point piecewise polynomial interpolation while the vibrational wavefunctions χ_w were obtained from the numerical solution of the Schrödinger equation for the nuclear motion in the most accurate adiabatic potential given by Schwartz and Le Roy [4]. These were subsequently used in equation (2) to calculate the rovibrational matrix elements of the multipole moments. All the calculations were performed using the computer program "LEVEL 6.0" obtained from Le Roy [5].

3. Results and discussion

Some of the adiabatic matrix elements for the heavier isotopomers of hydrogen molecule are given in Tables 1 and 2. The listing is restricted to only those matrix elements that are needed for the theoretical interpretation of the various infrared absorption features of these molecules in the solid phase. For the heteronuclear molecules, the contribution of the weak oscillating dipole-moment (Q_1) (engendered by the vibration of the molecule due to the break-down of the clamped nuclei approximation) to the Q_ℓ -moment becomes progressively smaller with increasing ℓ and is altogether neglected in the present calculations. Our quadrupole (Q_2) matrix elements agree with those of Hunt *et al* [5] to within 0.25%. Our results for the hexadecapole (Q_4) moment of D_2 differ by 2% and 3% for $v'=0$ and 1, respectively, from the

calculations of Karl *et al* [7]. The use of more accurate bond-length dependent multipole moment functions and better effective potential in the solution of the vibrational wavefunctions in the present calculation would suggest that the results reported here are more accurate. Previously Lo had estimated [8] some of the matrix elements of the higher moments Q_3 , Q_4 and Q_5 of HD using the known values of H_2 and making the necessary translation of the origin (from CC to CM). The estimated values are in close agreement with our results. As for the other higher order moments, the matrix elements are reported here for the first time.

Table 1. Rovibrational matrix elements $\langle 00|Q_\ell|v'\ell \rangle$ of the multipole moments Q_ℓ of HD, HT and DT molecules in atomic units (ea_0^ℓ)

v'	ℓ	$\langle 00 Q_\ell v'\ell \rangle$ for		
		HD	HT	DT
0	2	0.480 82	0.479 39	0.474 51
0	3	-0.351 41	-0.522 01	-0.203 93
0	4	0.501 61	0.711 50	0.369 95
0	5	-0.487 56	-0.853 80	-0.243 88
0	6	0.556 93	1.045 67	0.293 14
0	7	-0.590 06	-1.272 52	-0.235 45
0	8	0.655 74	1.565 00	0.245 85
0	9	-0.724 73	-1.944 83	-0.218 23
0	10	0.820 93	2.450 94	0.218 85
0	11	-0.941 88	-3.136 57	-0.206 40
1	2	0.074 07	0.072 37	0.065 67
1	3	-0.084 17	-0.122 21	-0.042 56
1	4	0.164 51	0.227 67	0.106 51
1	5	-0.200 94	-0.344 23	-0.088 90
1	6	0.274 33	0.505 27	0.128 95
1	7	-0.335 64	-0.712 27	-0.121 00
1	8	0.419 82	0.989 41	0.144 13
1	9	-0.771 72	-1.361 28	0.143 78
1	10	0.628 94	1.868 46	0.158 82
1	11	-0.511 74	-2.567 99	-0.163 29

Table 2. Rovibrational matrix elements $\langle 00|Q_\ell|v'\ell \rangle$ of the multipole moments Q_ℓ of D_2 and T_2 molecules in atomic units (ea_0^ℓ)

v'	ℓ	$\langle 00 Q_\ell v'\ell \rangle$ for		$\langle 01 Q_\ell v'\ell \rangle$ for	
		D_2	T_2	D_2	T_2
0	2	0.476248	0.472593	0.477334	0.473325
0	4	0.32014	0.31162	0.32247	0.31318
0	6	0.1978	0.1867	0.2006	0.1886
0	8	0.1227	0.1110	0.1254	0.1127
0	10	0.07922	0.06778	0.08170	0.06931

Table 2. (Cont'd)

v'	ℓ	$\langle 00 Q_\ell v'\ell\rangle$ for		$\langle 01 Q_\ell v'\ell\rangle$ for	
		D ₂	T ₂	D ₂	T ₂
1	2	0.0682331	0.0626071	0.0645577	0.0599116
1	4	0.10048	0.090933	0.095884	0.087594
1	6	0.09255	0.08197	0.08879	0.07928
1	8	0.07428	0.06371	0.07165	0.06188
1	10	0.05786	0.04751	0.05615	0.04637

By way of illustration of the use of these matrix elements, in Tables 3 and 4 we predict the theoretical intensities of zero-phonon single transitions in solid HD and D₂ and compare them with available experimental data. Note that for the heteronuclear isotopomers, the ortho-para distinction does not exist which implies that in the solid phase, practically all of the molecules are in the $v = 0, J = 0$ state. The formulas to calculate theoretical absorption coefficients for HD merit a brief comment. It can easily be shown that the general formulas developed by Balasubramanian *et al* [9] for the single transitions in para-H₂ ($J = 0$), in conjunction with the matrix elements reported in the present work, are also applicable for the heteronuclear varieties HD, HT and DT both for the even as well as odd values of ℓ . The validity of the above statement can be further confirmed by comparing the theoretical expressions of Tipping *et al* [10,11] for the integrated intensity of zero-phonon $T_v(0)$, $U_v(0)$ and $V_v(0)$ single transitions in solid HD with the corresponding formulas derived from the general expression of [9] using the transformed multipole moment Q_ℓ obtained from equation (3) in which the value of Δ for HD [as deduced from equation (4)] is set $\sim R/6$. In general, there is reasonable agreement among the present work, experimental observations and previous theoretical estimates. However, the full vindication of the reliability of the present results

may have to await new infrared measurements in solid D₂, T₂, HD, HT and DT, especially of the higher order multipole-induced transitions.

More details of calculated data can be seen in [17, 18].

 Table 4. Comparison of theoretical and experimental integrated absorption coefficient $\tilde{\alpha}$ of typical single and double zero-phonon transitions in solid D₂

Transition	Integrated absorption coefficient $\tilde{\alpha} / \text{m}^3\text{s}^{-1}$		Reference containing measurement data
	Theory	Experiment ^a	
$U_{0\leftarrow 0}(0)$	8.45×10^{-22}	1.1×10^{-21}	[15]
$S_{1\leftarrow 0}(0)$	2.12×10^{-21}	1.4×10^{-21}	[14]
$U_{1\leftarrow 0}(0)$	8.32×10^{-23}	$1.2 (0.2) \times 10^{-22}$ 8.3×10^{-23}	[16] [15]
$U_{1\leftarrow 0}(1)$	4.21×10^{-23}	$6.6 (2.0) \times 10^{-23}$	[16]
$S_{0\leftarrow 0}(0) + Q_{1\leftarrow 0}(0)$	5.75×10^{-20}	3.5×10^{-20}	[14]
$U_{0\leftarrow 0}(0) + Q_{1\leftarrow 0}(0)$	1.91×10^{-23}	$2.7 (0.8) \times 10^{-23}$	[16]

^aEstimated experimental error, wherever available, is given in brackets

4. Conclusion

Rovibrational matrix elements of multipole moments of the heavier isotopomers of hydrogen molecule have been computed and the results used to predict the integrated absorption coefficients of certain zero-phonon transitions in the infrared spectrum of solid HD and D₂. It is shown that the general intensity formulas developed by Balasubramanian *et al* [9] for single transitions in solid para-H₂ are equally applicable for the heteronuclear isotopomers of H₂ without any restriction on ℓ . New and accurate measurements of the infrared spectrum of solid hydrogens of heavier isotopomers are desirable.

 Table 3. Comparison of theoretical and experimental integrated absorption coefficient $\tilde{\alpha}$ of typical zero-phonon single transitions in solid HD

Transition	Integrated absorption coefficient $\tilde{\alpha} / \text{m}^3\text{s}^{-1}$				
	Experiment		Theory		
	Ref. [8]	Ref. [13]	Ref. [8]	Ref. [10,11]	This work
$T_{0\leftarrow 0}(0)$			1.58×10^{-21}	4.06×10^{-21}	3.94×10^{-21}
$U_{0\leftarrow 0}(0)$	1.2×10^{-21}	1.1×10^{-21}	1.50×10^{-21}	1.97×10^{-21}	1.86×10^{-21}
$V_{0\leftarrow 0}(0)$	1.1×10^{-22}	8.9×10^{-23}	1.29×10^{-22}	2.10×10^{-22}	1.96×10^{-22}
$T_{1\leftarrow 0}(0)$				2.44×10^{-22}	2.26×10^{-22}
$U_{1\leftarrow 0}(0)$	1.7×10^{-22}	1.5×10^{-22}	1.27×10^{-22}	2.22×10^{-22}	2.00×10^{-22}
$V_{1\leftarrow 0}(0)$	2.1×10^{-23}	2.1×10^{-23}	1.43×10^{-23}	3.77×10^{-23}	3.32×10^{-23}

References

- [1] A P Mishra and T K Balasubramanian *Mole. Phys.* **90** 895 (1997)
- [2] J Komasa and A J Thakkar *Mole. Phys.* **78** 1039 (1993)
- [3] C G Gray *Can. J. Phys.* **54** 505 (1976)
- [4] C Schwartz and R J Le Roy *J. Mole. Spectrosc.* **121** 420 (1987)
- [5] R J Le Roy *Chemical Physics Research Report CP-555* (Ontario : University of Waterloo) (1995)
- [6] J L Hunt, J D Poll and L Wolniewicz *Can. J. Phys.* **62** 1719 (1984)
- [7] G Karl, J D Poll and L Wolniewicz *Can. J. Phys.* **53** 1781 (1975)
- [8] K K Lo *PhD dissertation* The Ohio State University (1983)
- [9] T K Balasubramanian, R D'Souza, R D'Cunha and K Narahari Rao *J. Mole. Spectros.* **153** 741 (1992)
- [10] R H Tipping, J D Poll, S I Lee, T W Noh, S Y Lee and J R Gaines *Phys. Rev.* **B39** 6514 (1989)
- [11] R H Tipping, Q Ma, J D Poll, T W Noh, S Y Lee, S I Lee and J R Gaines *Phys. Rev.* **B38** 6440 (1988)
- [12] J D Poll, R H Tipping, S Y Lee, S-I Lee, T W Noh and J R Gaines *Phys. Rev.* **B39** 11, 372 (1989)
- [13] S Y Lee *PhD dissertation* The Ohio State University (1987)
- [14] A Crane and H P Gush *Can. J. Phys.* **44** 373 (1966)
- [15] S B Baliga, R Sooryakumar, K Narahari Rao, R H Tipping and J D Poll *Phys. Rev.* **B35** 9766 (1987)
- [16] M C Chan and T Oka *J. Chem. Phys.* **93** 979 (1990)
- [17] A P Mishra and T K Balasubramanian *Mole. Phys.* **98** 967 (2000)
- [18] A P Mishra, S V N Bhaskara Rao and T K Balasubramanian *Mole. Phys.* (In Press)