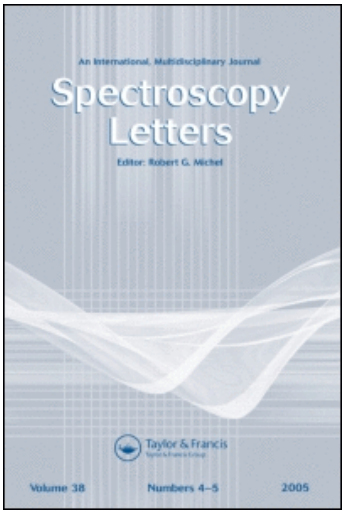

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On The Accuracy of The Vibrational Wave Functions and Derived Quantities

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ON THE ACCURACY OF THE VIBRATIONAL WAVE FUNCTIONS AND DERIVED QUANTITIES

Key words : Vibrational wave functions.

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ABSTRACT

Effect due to uncertainty in the dissociation energy, which is a major source of error (Jarmain, J. Quant. Spectr. Radiat. Transfer, (1971), 11, 421-6) in the calculations of vibrational wave functions and derived quantities, has been investigated. It has been found that for the molecules, for which the highest observed vibrational level is wall below the dissoci - ation limit, the effect is extremely small.

In the last decade vibrational wave functions for large number of diatomic spices have been computed numerically. The computer programme originally written by Cooley[1] and modified by Zare and Cashion[2], based on the method previously outlined by Hartee[3] is in wide use for this purpose. The accuracy of the results and the sources of error have been discussed in detail by Jarmain[4]. The accuracy of the wave functions was inves- tigated by three tests: (i) by comparing observed

vibrational eigenvalues with those generated by the programme, (ii) by comparing observed rotational energies with those generated by the programme and (iii) by calculating the orthogonality integrals or 'Noise factor defined by $\max_{v_1=v_2} \left| \int \psi_{v_1} \psi_{v_2} dr \right|^2$

According to Jarmain[4] the errors in the calculated quantities can be classified in two groups: (i) those that arise from errors or approximations in the method and (ii) those that stem from inaccurate experimental data.

(i) Errors of this kind are found to be insignificant.

(ii) Inadequate or incomplete experimental data represent a real limitation, especially if the dissociation energy, D_e, is not well established. In this circumstance the potential energy curve does not have the proper shape and there will be errors of unknown magnitudes in all derived quantities. It must be mentioned here that the dissociation energy enters in the extrapolation method suggested by Jarmain[4].

In the present communication we investigate the effect of uncertainty in D_e on the vibrational wave functions and derived quantities like vibrational and rotational energy and 'noise factor'.

The typical case under consideration is the ground state of SnF molecule. Three different values of the dissociation energy are available for this case: (i) 45000 cm^{-1}, Singh and Rai[5], (ii) 31748 cm^{-1}, Herzberg[6]

and (iii) 26909 cm^{-1}, Gaydon[7]. The RKR potential curve for this case has been reported by Singh and Rai[5] and we have used the same curve in the present study. In order to calculate the wave functions up to highest observed vibrational level (V_{max}= 8) in the present case) the potential curve was extrapolated both on right and left sides by the method suggested by Jarmain[4]. All the three values of D_e mentioned above were utilized in turn and calculations were carried out for each case. The calculations were performed on IBM 360 at the Physical Research Laboratory, Ahmedabad (India). Vibrational wave functions, vibrational energies, rotational energies and 'noise factors' were generated and examined in the context of the three tests described by Jarmain. Table (1) and (2) display the numerical results. It can be seen from the tables that the dissociation energy has a very small effect on the vibrational and rotational energies. The 'noise factor' in each case was found to be less than 10^{-14}.

To examine the effect of D_e, the extrapolated wings of the potential curve, with each value of D_e, were carefully examined. It was found that in an appreciable region beyond the turning points of the highest vibrational level the curves reproduced almost the same energy. In the regions where curves differ from each other the wave function values for the highest observed level were found to be extremely small

TABLE (1)

Comparison of experimental G(v) (cm^{-1}) with those generated by the Program

Vibrational quantum number	G(v) expt.	G(v) when D_e= 45000 cm^{-1}	Dev	G(v) when D_e=26909 cm^{-1}	Dev	G(v) when D_e=31748 cm^{-1}	Dev
0	290.8	290.8	0.0	290.8	0.0	290.8	0.0
1	868.1	868.5	+ 0.4	868.5	+ 0.4	868.5	+ 0.4
2	1440.2	1440.7	+ 0.5	1440.7	+ 0.5	1440.7	+ 0.5
3	2006.4	2007.6	+ 1.2	2007.6	+ 1.2	2007.6	+ 1.2
4	2567.8	2568.4	+ 0.6	2568.4	+ 0.6	2568.4	+ 0.6
5	3123.4	3123.5	+ 0.1	3123.6	+ 0.2	3123.6	+ 0.2
6	3674.2	3674.2	0.0	3674.4	+ 0.2	3674.3	+ 0.1
7	4219.8	4219.5	- 0.3	4219.9	+ 0.1	4219.8	+ 0.3
8	4760.8	4761.5	+ 0.7	4762.6	+ 1.8	4762.2	+ 0.7

TABLE (2)

Comparison of experimental B_v(cm^{-1}) values with those generated by the Program

Vibrational quantum number	B_v expt.	B_v when D_e=45000 cm^{-1}	Dev	B_v when D_e=26909 cm^{-1}	Dev	B_v when D_e=31748 cm^{-1}	Dev
0	0.2722	0.2723	+0.0001	0.2723	+0.0001	0.2723	+0.0001
1	0.2710	0.2710	0.0000	0.2710	+0.0000	0.2710	0.0000
2	0.2699	0.2699	0.0000	0.2699	0.0000	0.2699	0.0000
3	0.2689	0.2689	0.0000	0.2689	0.0000	0.2689	0.0000
4	0.2678	0.2679	+0.0001	0.2679	+0.0001	0.2679	+0.0001
5	0.2667	0.2669	+0.0002	0.2669	+0.0002	0.2669	+0.0002
6	0.2656	0.2655	-0.0001	0.2656	0.0000	0.2656	0.0000
7	0.2645	0.2641	-0.0004	0.2642	-0.0003	0.2642	-0.0003
8	0.2634	0.2630	-0.0004	0.2630	-0.0004	0.2632	-0.0002

($\sim 10^{-10}$) to produce any sizable effect on the final quantities. The wave functions for the lower vibrational levels were still smaller in the regions of extrapolation.

The results of the present investigation clearly show that for the molecules for which the highest observed energy level lies well below the dissociation limit, the effect of D_e, used in the extrapolation of the potential curve will be extremely small. In such cases the uncertain values of D_e will also give the reasonably accurate values of the wave functions and the derived quantities.

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