

Photodissociation of NaH using time-dependent Fourier grid method

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Abstract. We have solved the time dependent Schrödinger equation by using the Chebyshev polynomial scheme and Fourier grid Hamiltonian method to calculate the dissociation cross section of NaH molecule by 1-photon absorption from the $X^1\Sigma^+$ state to the $B^1\Pi$ state. We have found that the results differ significantly from an earlier calculation [1] although we have used the same set of potential energy curves [2].

Keywords. Photodissociation; molecules; interaction of photon with molecules.

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1. Introduction

Photodissociation is one of the channels for destruction of the alkali hydride molecules like NaH and LiH in interstellar clouds [1]. Photodissociation cross section of NaH from the $v'' = 0$ level of the ground state ($X^1\Sigma^+$) to the excited $B^1\Pi$ state has been calculated previously by Kirby and Dalgarno [1] using conventional method. In this work we have done time-dependent quantum mechanical calculations for the photodissociation cross section of NaH molecule via the $B^1\Pi$ state from the $v'' = 0$ level of the ground $X^1\Sigma^+$ state. Time-dependent Schrödinger equation has been solved using Fourier grid Hamiltonian method [3,4] and the Chebyshev polynomial scheme [5] has been used for time propagation. The photodissociation cross section for NaH molecule in a wide range of photon energy was obtained from a single calculation by the Fourier transformation of the autocorrelation function over time [4,6]. We have done the calculation for the photodissociation cross section by using the same set of potential energy curves [1] and the same set of dipole transition moments [7] as used in the previous calculation [1]. But the photodissociation spectrum obtained in this calculation is widely different from that obtained previously [1]. We found that the maximum value of the photodissociation cross section is 3.621 \AA^2 and the photon energy at which the photodissociation cross section is maximum is 33404 cm^{-1} whereas in the previous calculation [1] the respective values for the maximum cross section and the corresponding photon energy were 2.4 \AA^2 and 36817 cm^{-1} . In the previous calculation [1], it was reported that the potential curves [1] for the $X^1\Sigma^+$ and the $B^1\Pi$ state have

been rearranged to make the threshold of photodissociation from $v'' = 0$ of $X^1\Sigma^+$ state to be 4.17 eV without mentioning how they have rearranged the curves. For the curves of Sachs *et al* [2], the threshold for photodissociation from $v'' = 0$ of the $X^1\Sigma^+$ state is 3.879 eV. To make this threshold to be 4.17 eV, we have rearranged the curves in two ways (see §3). We found that even for these two calculations, our results are significantly different from Kirby and Dalgarno. Results with other sets of curves [8,9] will be reported elsewhere.

2. Theory

Let the molecule be in a bound vibrational level of its ground electronic state. The wave function ψ can be obtained by Fourier grid Hamiltonian method [3,4]. In this method, potential energy is treated in coordinate space while kinetic energy is treated in momentum space.

The molecule is excited to a higher electronic state upon absorbing a photon. Let μ be the transition dipole moment associated with this transition. An initial wavepacket is constructed as

$$\Phi(R, t = 0) = \mu(R)\psi(R, E_i), \quad (1)$$

where R is the internuclear separation and E_i is the energy of the initial vibrational state. This wavepacket is propagated in time under the influence of the excited state potential to give the time-dependent wavepacket. This is done using Chebyshev scheme for time propagation [5]. Time dependent wavepacket is evaluated at a series of time steps. At each time step, autocorrelation function is computed, till it converges to a very small value

$$F(t) = \langle \Phi(R, t = 0) | \Phi(R, t) \rangle. \quad (2)$$

The total absorption cross section is found by Fourier transform of the autocorrelation function over time [4,6]

$$\sigma_i^{\text{Tot.}}(\nu) = \frac{\pi\nu}{3c\epsilon_0\hbar} \int_{-\infty}^{\infty} e^{\frac{iEt}{\hbar}} F(t) dt, \quad (3)$$

where

$$E = E_i + h\nu. \quad (4)$$

In the time integration, instead of ∞ the upper limit is put as the time when the autocorrelation function converges sufficiently.

Now, the grids in coordinate space are finite in length. Complications in calculations may arise due to the nature of the fast Fourier transform technique which describes periodic functions [10]. If the wave function has a finite value at the edge of the grid, this finite value is reflected back changing the result drastically. To solve this problem, an artificial negative potential is added to the Hamiltonian. This is non-zero only near the edges of the grid and gradually annihilates the wavepacket as it comes in contact with it. Here, damping factor at the I th grid point is of the form

$$DF = -2i \times \left[\frac{(I - N_d)}{(N - N_d)} \right]^3 \times Z_{\min}, \quad (5)$$

where N_d is the grid point from which damping starts, N is the total number of grid points, Z_{\min} is a constant factor. Z_{\min} and N_d can be determined by the method described in Vibok *et al* [10].

3. Calculations

We have used the one-dimensional Fourier grid program of Balint-Kurti to find the photodissociation cross section by solving the time-dependent Schrödinger equation. We have done three sets of calculations in the following ways:

(1) *Set I*: Potential energy curves for the $X^1\Sigma^+$ and $B^1\Pi$ states were used as obtained in the literature [2] (see figure 1).

In the previous calculation [1], Kirby and Dalgarno have rearranged the curves of Sachs *et al* [2] (without mentioning how they have rearranged) to make the dissociation threshold 4.17 eV from the $v'' = 0$ level of the ground state. Here we have rearranged the curves in the following two ways to make the dissociation threshold 4.17 eV.

(2) *Set II*: We have shifted the asymptotic limit of the ground state $X^1\Sigma^+$ of Sachs *et al* [2] upwards so that the dissociation energy of the ground state from $v'' = 0$ is 2.05 eV. We have also parallelly shifted the excited state upwards with respect to the ground state, so that the photodissociation threshold (from $v'' = 0$ level of the ground $X^1\Sigma^+$ state to the asymptote of the excited state) is 4.17 eV.

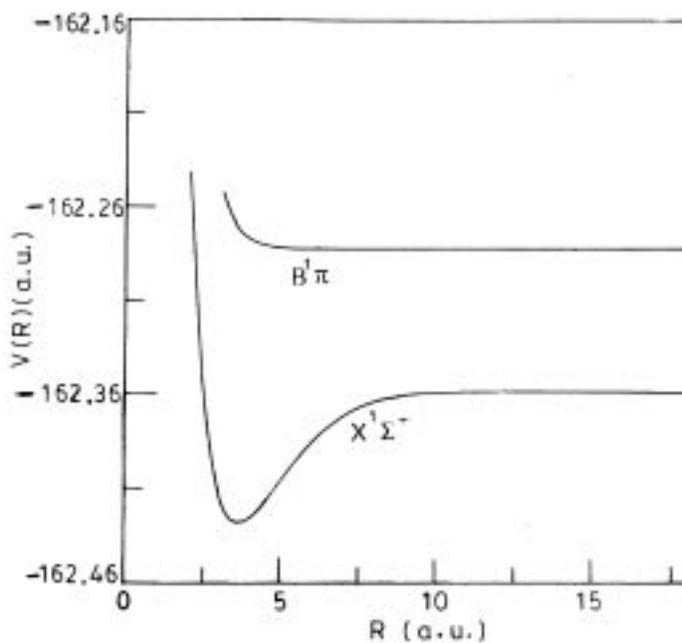


Figure 1. Potential energy curves for the ground state $X^1\Sigma^+$ and the excited state $B^1\Pi$ of NaH, reproduced from Sachs *et al* [2].

(3) *Set III*: We have shifted the excited state upwards with respect to the ground state (without changing the curves) such that the threshold for dissociation is 4.17 eV.

For all these calculations, dipole transition moments of Sachs *et al* [7] have been used. Grid spacing was taken to be 0.05 a.u for all three sets of calculations. We have tried different values of time step for propagation, and presented results for time step 6.5 a.u which gives the best energy convergence.

4. Results and discussion

The maximum cross section and the corresponding photon-energy for all the three sets of calculations mentioned in the previous section have been tabulated (table 1) along with the results of Kirby and Dalgarno [1].

We found that the results of our calculation are significantly different from the previous result [1]. For the first set of calculation where we have used the potential curves without rearranging them, the value of maximum cross section is 3.621 \AA^2 and the corresponding photon energy is 33404 cm^{-1} . But the maximum cross section in the previous calculation is much lower (2.4 \AA^2) and corresponding photon energy is much higher (36817 cm^{-1}). It may be argued that this difference is due to the differences in the dissociation threshold as is given in column 4 of table 1. But in sets II and III, the dissociation threshold energy is the same as in the previous calculation [4] i.e. $\sim 4.17 \text{ eV}$, and even then this difference is more than 1000 cm^{-1} . The maximum values of photodissociation cross section for these sets are even higher. We got almost identical results, since we have used almost the same set of curves. Hence the spectrum for sets II and III coincide, as seen in figure 2 (solid curve). For all these calculations, we find that the difference in threshold energy (table 1) results in a shift in the spectrum and hence the position of maximum cross section is shifted as shown in figure 2. The position of maximum cross section has been shown by dashed vertical lines. Starting from left, the first line corresponds to set I, the second one to sets II and III and the third one shows the position of maximum photodissociation cross section obtained by Kirby and Dalgarno [1]. We find that the photon energy corresponding to the maximum cross section is close to the transition at the equilibrium separation. The photon energy is slightly less than the energy difference at the equilibrium separation for all these calculations and the difference lies within 130 and 159 cm^{-1} . Subtracting the energy in

Table 1.

Set	Maximum cross section (\AA^2)	Photon energy for maximum cross section from $v' = 0$ (cm^{-1})	Threshold* for dissociation from $v' = 0$ (cm^{-1})	Energy difference of $B^1\Pi$ at r_e from $v' = 0$ (cm^{-1})
I	3.621	33404	31289	33563
II	3.8757	35763	33633	35900
III	3.876	35772	33634	35902
Ref. [4]	2.4	36817	33633	

*Threshold for dissociation from r_e can be obtained by adding column 2 of table 2 to this column.

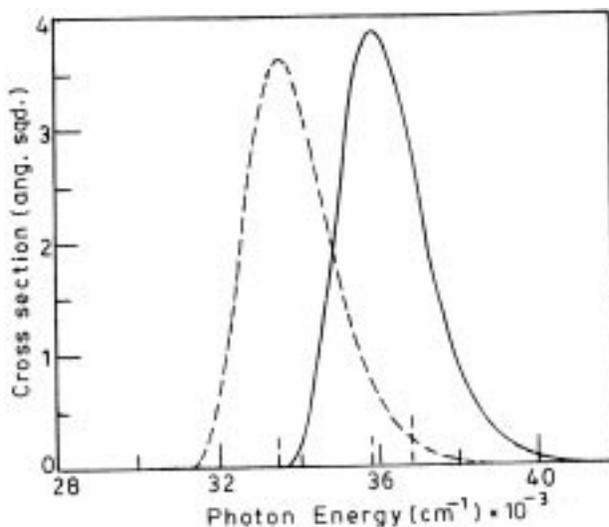


Figure 2. Photodissociation cross section of NaH molecule as a function of photon energy for different sets of potential energy curves ($X^1\Sigma^+$ and $B^1\Pi$). Dashed line: results for set I (see §3); solid line: results for sets II and III (see text).

Table 2.

Set	Zero-point energy (cm^{-1})	Energy difference at r_{\min}^* (cm^{-1}) (r_{\min} in a.u.)	Energy difference at r_{\max}^* (cm^{-1}) (r_{\max} in a.u.)
I	543	35520 (3.32)	32338 (3.99)
II	543	37863 (3.32)	34740 (3.99)
III	543	37865 (3.32)	34742 (3.99)

* r_{\min}^* and r_{\max}^* are the inner and outer turning points of the ground vibrational level of the ground $X^1\Sigma^+$ state.

column 4 from that in column 3 of table 2, one can get the range of photon energy within which the Franck–Condon transitions can occur. We find that the maximum of the cross section lies well within this Franck–Condon region.

For set II, shift in the ground state asymptote has negligible effect on the position of the ground vibrational level, from the minimum of the potential energy curve (table 2).

5. Conclusions

We obtained the photodissociation cross section of NaH from the ground $X^1\Sigma^+$ state via the excited state $B^1\Pi$. We have found that our results are significantly different from those obtained by Kirby and Dalgarno [1].

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