

## Reexamination of the photodissociation of NaH

Swaralipi Ghosh, S. S. Bhattacharyya, and Samir Saha\*

*Atomic and Molecular Physics Section, Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India*

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We have recalculated the photodissociation cross section of NaH as a function of photon wavelength for the  $X^1\Sigma \rightarrow B^1\Pi$  transition using the time-independent Fermi golden rule. We have made an attempt to clarify the discrepancy between a recent calculation where the time-dependent autocorrelation function was employed and an earlier one where the Fermi golden rule was used.

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In a recent paper, Bhattacharjee and Rai Dastidar [1] have computed the photodissociation cross section of NaH from the  $v=0$  level of the ground  $X^1\Sigma$  state to the excited  $B^1\Pi$  state employing an “unconventional” [2] time-dependent autocorrelation function formula. Earlier, Kirby and Dalgarno [3] had calculated the photodissociation cross sections of NaH and LiH from the  $v=0, J=0$  level of the  $X^1\Sigma$  state to the  $B^1\Pi$  state using the conventional Fermi golden rule. Bhattacharjee and Rai Dastidar [1] have used various sets of potential energies for the  $X$  and  $B$  states with different values of the dissociation threshold, whereas Kirby and Dalgarno [3] used the potential energies and transition dipole moment from Sachs *et al.* [4] and experimental value (4.17 eV) of the dissociation threshold given by Gaydon [5]. Bhattacharjee and Rai Dastidar [1] have found that the value of the maximum photodissociation cross section of NaH and the corresponding photon energy are significantly different from those given by Kirby and Dalgarno [3]. They could not explain this difference.

We have recalculated the photodissociation cross section of NaH using the simple Fermi golden rule formula

$$\sigma = g_{\Lambda'\Lambda} \left( \frac{12.25}{\lambda} \right) |Q_{\Lambda v J}^{\Lambda' E' J'}|^2, \quad (1)$$

where the degeneracy factor  $g_{\Lambda'\Lambda}$  is [6]

$$g_{\Lambda'\Lambda} = \frac{2 - \delta_{0\Lambda} \delta_{0\Lambda'}}{2 - \delta_{0\Lambda}} \quad (2)$$

and the bound-free matrix element  $Q_{\Lambda v J}^{\Lambda' E' J'}$  is [6]

$$Q_{\Lambda v J}^{\Lambda' E' J'} = \langle \chi_{\Lambda' E' J'}(R) | Q(R) | \chi_{\Lambda v J}(R) \rangle. \quad (3)$$

Here  $Q(R)$  is the transition dipole moment and  $\chi_{\Lambda' E' J'}(R)$  is normalized in the energy space as [2,7]

$$\chi_{\Lambda' E' J'}(R) \underset{R \rightarrow \infty}{\sim} (2\mu/\pi k')^{1/2} \sin \left( k'R - \frac{J'\pi}{2} + \eta_{J'} \right). \quad (4)$$

Here  $\mu$  is the reduced mass,  $k' = \sqrt{2\mu E'}$ ,  $E'$  being the photofragmentation energy, and  $\eta_{J'}$  is the phase shift. In Eq.

(1),  $\sigma$  is in  $\text{\AA}^2$  and  $\lambda$  is in  $\text{\AA}$ . All other quantities in Eqs. (1), (3), and (4) are in (Hartree) atomic units. Our expression for  $\sigma$  is the same as that given by Kirby and Dalgarno [3] where the continuum wave function  $\chi_{\Lambda' E' J'}(R)$  was normalized in the momentum space [8].

We have taken the potential energies and the transition dipole moment from Sachs *et al.* [4], and the experimental value (4.17 eV) of the dissociation threshold as used by Kirby and Dalgarno [3]. We have obtained *almost* the same values of the maximum cross section ( $4.06 \text{\AA}^2$ ) and the corresponding photon energy ( $35714 \text{ cm}^{-1}$ ) as given by Bhattacharjee and Rai Dastidar [1] for sets V and VI in their paper, where the potential energies are from Sachs *et al.* [5] with some alternations but the dissociation threshold energy is 4.17 eV. The slight difference in our maximum photodissociation cross section and the corresponding photon energy from those for sets V and VI of Bhattacharjee and Rai Dastidar [1] is due to the fact that the potential energies of Sachs *et al.* [4] are slightly altered because of shifting of the ground-state asymptote and/or excited state, by the authors of Ref. [1], to make the dissociation threshold 4.17 eV. It may be mentioned here that the maximum cross section and the corresponding photon energy do not depend much on the potential energies but are very sensitive to the dissociation threshold energy. This is discernible from the results for sets I and V (VI) in Table I of their paper [1], where the potential energies are slightly different but the dissociation threshold differs appreciably. Here the results are much different, but in sets V and VI where the potential energies are slightly altered (due to shifting in different ways) while the dissociation threshold is the same, the results are hardly affected.

In the paper by Bhattacharjee and Rai Dastidar [1], there is no mention whether they have taken into account the rotational transition ( $J=0 \rightarrow J'=1$ ) and the degeneracy factor (2 for  $\Sigma \rightarrow \Pi$  transition) as considered by Kirby and Dalgarno [3]. Also, there is an error in the cross section formula given by them. The symbol  $\nu$  used in their formula is defined as the angular frequency (i.e.,  $2\pi\nu$ ) by Eq. (4) in their paper [1]. The correct formula should be [2,9]

$$\sigma = g_{\Lambda'\Lambda} \left( \frac{\pi\nu}{3c\epsilon_0} \right) \int_{-\infty}^{+\infty} e^{iEt} F(t) dt \quad (5)$$

in atomic units, where  $g_{\Lambda'\Lambda}$  is the degeneracy factor for transition from electronic state  $\Lambda$  to  $\Lambda'$  [Eq. (2)] and  $\nu$  is the

\*Electronic address: msscs@mahendra.iacs.res.in

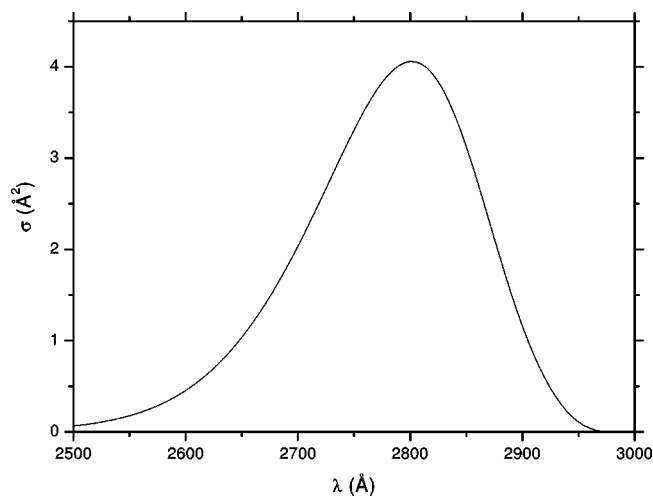


FIG. 1. The photodissociation cross section  $\sigma$  of NaH as a function of photon wavelength  $\lambda$  for the  $X^1\Sigma \rightarrow B^1\Pi$  transition using the same potential energies, transition dipole moment, and dissociation threshold as taken by Kirby and Dalgarno [3].

photon frequency ( $\nu=c/\lambda$ ). The cross sections obtained in Ref. [1] are, however, correct because in the (one-dimensional) time-dependent program of Balint-Kurti used, the rotational effect along with the degeneracy factor has been taken into account in the (correct) expression for the

cross section. It is worth mentioning here that, following Heller [2], the cross section formula involving autocorrelation function  $F(t)$  in Eq. (5) can be derived from that in Eq. (1).

The results computed by Bhattacharjee and Rai Dastidar [1] did not agree with those of Kirby and Dalgarno [3] as the  $\sigma$ - $\lambda$  curve (Fig. 1) for NaH in their paper [3] may have an insufficient number of ( $\sigma$ - $\lambda$ ) data, mainly in the peak region. The curve is also misplotted, the  $x$  axis ( $\lambda$ ) has somehow been reversed. The curve should follow the expected pattern with the tail towards the lower wavelength ( $\lambda$ ) side as in the  $\sigma$ - $\lambda$  curve (Fig. 2) for LiH in their paper. The inaccuracy of Fig. 1 in the paper [3] is also evident from a look at our present Fig. 1, where our computed cross section  $\sigma$  of NaH against photon wavelength  $\lambda$  has been plotted. We assume that Kirby and Dalgarno [3] have obtained the maximum photodissociation cross section ( $2.4 \text{ \AA}^2$ ) and the corresponding photon wavelength ( $2715 \text{ \AA}$ ) from the wrongly plotted ( $\sigma$ - $\lambda$ ) curve. Hence, incorrect results were reported. It is important to note that from their formula (which is correct) one obtains  $\sigma=2.4 \text{ \AA}^2$  at  $\lambda=2715 \text{ \AA}$  which is of course not the maximum cross section at the corresponding wavelength. We find that with the same potential energies, transition dipole moment and the dissociation threshold as taken by Kirby and Dalgarno [3], the maximum photodissociation cross section for NaH is  $4.06 \text{ \AA}^2$  and the corresponding photon wavelength is  $2800 \text{ \AA}$ .

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