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Photodissociation of NaH

Anindita Bhattacharjee and Krishna Rai Dastidar
Department of Spectroscopy, Indian Association for the Cultivation of Science, Calcutta 700032, India

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We have calculated the photodissociation cross section of NaH through the $B\,^1\Pi$ state. We have solved the time-dependent Schrödinger equation by using the Chebyshev-polynomial scheme and Fourier grid Hamiltonian method. We have used four different sets of potential-energy curves for $X\,^1\Sigma^+$ and $B\,^1\Pi$ states [E. S. Sachs, J. Hinze, and N. H. Sabelli, J. Chem. Phys. **62**, 3367 (1975); R. E. Olson and B. Liu, J. Chem. Phys. **73**, 2817 (1980); W. C. Stwalley, W. T. Zemke, and S. C. Yang, J. Phys. Chem. Ref. Data **20**, 156 (1991)]. We have found that the values of maximum photodissociation cross section and the corresponding photon energy depend on the choice of the potential-energy curves. But all these results differ significantly from an earlier calculation [K. Kirby and A. Dalgarno, Astrophys. J. **224**, 444 (1978)]. We have also found that the photodissociation occurs mainly due to the Franck-Condon transitions.

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I. INTRODUCTION

It is well known that the alkali hydride molecules, such as LiH and NaH are of astrophysical importance and the photodissociation is one of the channels for the destruction of these alkali hydride molecules in interstellar clouds [4]. In the present work we have studied the photodissociation of NaH molecule via $B\,^1\Pi$ state from the ground $X\,^1\Sigma^+$ state.

The calculation of 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 previously been done by Kirby and Dalgarno [4] using a conventional method. In this work we have solved the time-dependent Schrödinger equation by using the Fourier grid Hamiltonian method [5,6]. Chebyshev-polynomial scheme [7] has been used for the time propagation of the wave packet and 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 [6,8]. Photodissociation cross section for the transition from $X\,^1\Sigma^+$ ($v''=0$) ground state to $B\,^1\Pi$ state has been calculated by using the same set of potential-energy curves [1] and the same set of dipole transition moments [9] as used in the previous calculation [4]. But the photodissociation spectrum obtained in this calculation is significantly different from that obtained previously [4]. Therefore, we took this project to study the photodissociation spectrum of NaH by considering different sets of potential-energy curves [1–3] and found that the dissociation spectrum depends on the choice of potential-energy curves. We have done four sets of calculations with four pairs of potential-energy curves for $X\,^1\Sigma^+$ and $B\,^1\Pi$ as given in the literature [1–3]. We found that the maximum value of the photodissociation cross section varies from 3.39 to 3.69 Å^2 and the photon energy at which the photodissociation cross section is maximum varies from 33 404 to 34 401 cm^{-1}. But these results are widely different from the values obtained in the previous calculation [4], i.e., 2.4 Å^2 for the maximum cross section and 36 817 cm^{-1} for the corresponding photon energy. In the previous calculation [4], 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 the curves have been rearranged. We have found that for this set of curves [1] (unaltered), the threshold for photodissociation from $v''=0$ of the $X\,^1\Sigma^+$ state is 3.879 eV. Therefore to make this threshold to be 4.17 eV, we have rearranged the curves in two ways and found that even for these two calculations, our results are significantly different from Kirby and Dalgarno. We have also shown that the photodissociation occurs mainly due to the Franck-Condon transitions from the ground vibrational level of the ground state to the vibrational continuum of the repulsive $B\,^1\Pi$ state and the maximum photodissociation occurs due to the transition at the internuclear separation very close to the equilibrium value of the ground state.

II. THEORY

Let the molecule be in a bound rovibrational level of its ground electronic state. The wave function ψ can be obtained by the Fourier grid Hamiltonian method [5,6]. It is excited to a higher electronic state upon absorbing a photon. Let μ be the transition dipole moment associated with this transition. An initial wave packet can be constructed as

$$\Phi(R,t=0)=\mu(R)\psi(R,E_i), \tag{1}$$

where R is the internuclear separation and E_i is the energy of the initial vibrational state. This wave packet is propagated in time under the influence of the excited state potential to give the time-dependent wave packet. This is done using Chebyshev scheme for time propagation [7]. The time-dependent wavepacket is evaluated at a series of time steps. At each time step, autocorrelation function

$$F(t)=\langle\Phi(R,t=0)|\Phi(R,t)\rangle \tag{2}$$

is computed until it converges to a very small value. The total absorption cross section is found by Fourier transform of the autocorrelation function over time [6,8],

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

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where,

$$E = E_i + \hbar \nu. \tag{4}$$

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

The theory for the Fourier grid Hamiltonian method and the Chebyshev scheme for time propagation is described briefly below.

A. Fourier grid method

For a particle of mass m moving in one dimension under the influence of potential V, the nonrelativistic Hamiltonian is given [5,6] as

$$\hat{H} = \hat{T} + \hat{V}(x), \tag{5}$$

where $\hat{T}(=\hat{p}^2/2m)$ and $\hat{V}(x)$ are kinetic and potential energies, respectively. The potential-energy operator is diagonal in the coordinate representation while the kinetic-energy operator is diagonal in the momentum representation. Using Fourier transform, in coordinate representation, matrix element of the Hamiltonian operator can be written as

$$\langle x|\hat{H}|x'\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik(x-x')}T_k dk + V(x)\,\delta(x-x'). \tag{6}$$

To solve the Schrödinger equation using Fourier grid method, one has to replace the continuous range of coordinate values x by a uniform grid of N discrete values x_n given by

$$x_n = n\Delta x,$$

where Δx is uniform grid spacing and the length of the grid is $L = N\Delta x$.

The grid spacing in momentum space is

$$\Delta k = \frac{2\pi}{L} \tag{7}$$

and the momentum values at grid points in momentum space are

$$k_n = n\Delta k - k_{\mathrm{min},}\,. \tag{8}$$

where $k_{\mathrm{min}} = N\pi/L$.

The discretized identity and orthogonality relations are

$$\hat{I}_x = \sum_{n=1}^{N} |x_n\rangle \Delta x \langle x_n|, \tag{9a}$$

$$\Delta x \langle x_n|x_l\rangle = \delta_{nl.} \tag{9b}$$

The renormalized Hamiltonian matrix using the above relations is then given by

$$H^o_{ij} = \frac{1}{N}\left[\left\{\sum_{l=1}^{n-1} 2\cos\left(\frac{l2\pi(i-j)}{N}\right)T_l\right\} + (-1)^{(i-j)}T_{N/2}\right] + V(x_i)\,\delta_{ij}, \tag{10}$$

where

$$T_l = \frac{\hbar^2}{2m}\left(\frac{\hbar\pi l}{N\Delta x}\right)^2. \tag{11}$$

Expectation value of energy

$$E = \frac{\sum_{ij} \psi_i^* H^o_{ij} \psi_j}{\sum_i |\psi_i|^2}.$$

Minimizing E with respect to ψ_i gives a set of equations

$$\sum_j \left[H^o_{ij} - E_\lambda \delta_{ij}\right]\psi_j^\lambda = 0. \tag{12}$$

Solving these equations we can find the bound-state eigenvalues and eigenfunctions.

B. Time propagation

Time evolution of ψ is given by

$$\psi(t) = \exp\left[\frac{-i}{\hbar}\int_0^t \hat{H}dt\right]\psi(0). \tag{13}$$

For time propagation total time is divided into short intervals Δt in which the Hamiltonian does not change significantly. In Chebyshev-polynomial scheme, a polynomial expansion of the time-evolution operator is used using Chebyshev polynomials whose ranges are from $-i$ to i. So the Hamiltonian operator has to be renormalized by dividing it by ΔE. Also for maximum efficiency, range of eigenvalues are positioned from -1 to $+1$ by shifting the Hamiltonian to

$$\hat{H}_{\mathrm{norm}} = 2\,\frac{\hat{H} - \hat{I}(\frac{1}{2}\Delta E + V_{\mathrm{min}})}{\Delta E}, \tag{14}$$

where $\hat{H}$ is the original Hamiltonian, $\hat{I}$ is the identity, ΔE is the range of eigenvalues, and V_{min} is the lower bound of the potential energy. Hence the time evolution of ψ is given by

$$\psi(t) = \exp\left[\left(\frac{-i}{\hbar}\right)\left(\frac{\Delta E}{2} + V_{\mathrm{min}}\right)t\right]\sum_{n=0}^{N} a_n\left[\frac{\Delta E\Delta t}{2\hbar}\right] \times \Phi_n[-i\hat{H}_{\mathrm{norm}}]\psi(0), \tag{15}$$

where Φ_n are Chebyshev polynomials. Expansion coefficients are given by

$$a_n(\alpha) = \int_{-1}^{1} \frac{e^{i\alpha x}\Phi_n(x)dx}{(1-x^2)^{1/2}} = 2J_n(\alpha) \tag{16}$$

TABLE I. Maximum photodissociation cross section of NaH and the position of the maximum cross section in the photodissociation spectrum for six sets of calculations.

Set	Max. cr. sn. (Å^2)	Corr. photon energy from $v''=0$ (cm^{-1})	Threshold[a] for dissn. from $v''=0$ (cm^{-1})	Energy diff. of $B\,^1\Pi$ at r_e from $v''=0$ (cm^{-1})
I	3.621	33 404	31 289	33 563
II	3.597	33 867	31 975	33 997
III	3.394	34 401	32 021	34 529
IV	3.693	34 276	32 383	34 286
V	3.8757	35 763	33 633	35 900
VI	3.876	35 772	33 634	35 902
Ref. [4]	2.4	36 817	33 633	

[a] Threshold for dissociation from r_e can be obtained by adding column 2 of Table II to this column.

and $a_0(\alpha)=J_0(\alpha)$, with $\alpha=\Delta E\Delta t/2\hbar$.

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 that 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 nonzero only near the edges of the grid and gradually annihilates the wave packet as it comes in contact with it.

III. CALCULATIONS

To calculate the photodissociation cross section we have used the one-dimensional program for solving the time-dependent Schrödinger equation of Balint-Kurti, with some modifications. We have done six sets of calculations using different sets of potential-energy curves. In the first four sets, potential-energy curves for the $X\,^1\Sigma^+$ and $B\,^1\Pi$ states were used as obtained in literature [1–3] and in the last two sets (V and VI), we have rearranged the curves of Sachs, Hinze, and Sabelli [1] to make the dissociation threshold 4.17 eV from the $v''=0$ level of the ground $X\,^1\Sigma^+$ state. We have done the calculations for the following sets of curves for $X\,^1\Sigma^+$ and $B\,^1\Pi$ states.

(1) Set I. We have used the MCSCF potential-energy curves for the $X\,^1\Sigma^+$ and the $B\,^1\Pi$ states of Sachs, Hinze, and Sabelli [1].

(2) Set II. $X\,^1\Sigma^+$ and $B\,^1\Pi$ potential-energy curves from *ab initio* calculations of Olson and Liu [2] have been used.

(3) Set III. We have used the RKR curve for the $X\,^1\Sigma^+$ state recommended by Stwalley, Zemke, and Yang [3] and the $B\,^1\Pi$ curve of Sachs, Hinze, and Sabelli [1] keeping the energy difference between the two asymptotes same as in Ref. [1].

(4) Set IV. We have used the $B\,^1\Pi$ curve from Olson and Liu [2] and the RKR-potential-energy curve for the $X\,^1\Sigma^+$ state [3] keeping the energy difference between the two asymptotes same as in Ref. [2].

In the previous calculation [4], Kirby and Dalgarno have rearranged the curves of Sachs, Hinze, and Sabelli [1] (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.

(5) Set V. We have shifted the asymptotic limit of the ground state $X\,^1\Sigma^+$ of Sachs, Hinze, and Sabelli [1] 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.

(6) Set VI. 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 the six sets of calculations, dipole transition moments of Sachs, Hinze, and Sabelli [9] have been used.

For each set, we have repeated the calculation for different total time and checked for the convergence in energy, i.e., the difference in energy at the initial and the final time steps as well as the ratio of autocorrelation functions at the final and initial time steps. For each set, we have presented the results for the total time for which these two quantities are minimum. For the results of set I, the values of the convergence in energy and the ratio of final to initial autocorrelation functions are 9×10^{-9} and 4.2×10^{-7} a.u., respectively, and these values set the limits of accuracy in this calculation. We have also found that for calculations with different total times, the maximum variation in the values of maximum cross section is 5×10^{-4} Å^2 for set I. For the other sets, the accuracy limit is of the same order.

We have also calculated the Franck-Condon factors for transitions around the maximum of the cross section for set I and set II. In the first set, we have calculated the Franck-Condon factors for the transition from the $v''=0$ level of the $X\,^1\Sigma^+$ state to the continuum of the $B\,^1\Pi$ state in the range of photon energy from 4.085 to 4.167 eV on a grid of spacing 0.0272 eV. Similarly for the second set, same calculation has been done in the range of photon energy 4.127–4.182 eV on the grid of spacing 0.0272 eV. To calculate the Franck-Condon factors we have used Numerov's method for solving the radial Schrödinger equation to compute the bound and continuum wave functions.

IV. RESULTS AND DISCUSSION

The maximum cross section and the corresponding photon energy for all the six sets of calculations mentioned in

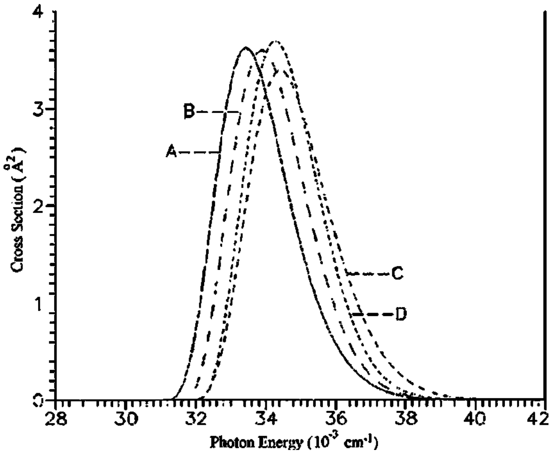

FIG. 1. Photodissociation cross section of the NaH molecule as a function of photon energy for different combinations of potential-energy curves ($X\,^1\Sigma^+$ and $B\,^1\Pi$). (A) Set I (see text): Both curves are from Sachs, Hinze, Sabelli [1]. (B) Set II (see text): Both curves are from Olson and Liu [2]. (C) Set III (see text): Ground state $X\,^1\Sigma^+$ is from Stwalley *et al.* [3] and $B\,^1\Pi$ state is from Sachs *et al.* [1]. (D) Set IV (see text): Ground state is from Stwalley, Zemke, and Yang [3], and $B\,^1\Pi$ state is from Olson and Liu [2].

the preceding section have been tabulated (Table I) along with the results of Kirby and Dalgarno [4].

We find that the results of our calculation are significantly different from the previous result [4]. For the first four sets of calculations, where we have used the potential curves without rearranging them, we got different values of photon energies for maximum cross section but the maximum difference is approximately 1000 cm^{-1}. Whereas the photon energy for maximum cross section obtained in the previous calculation [4] is widely different from ours, the difference lies within 2400–3400 cm^{-1} approximately. One may argue that this difference is due to the differences in the threshold values of dissociation energies (column 4 of Table I). But in set V and set VI, the dissociation threshold energy is the same as in the previous calculation [4], i.e., ~4.17 eV, even then this difference is more than 1000 cm^{-1}. The values of the maximum cross section obtained in our calculations are close to each other and varies from 3.394 to 3.693 Å^2, which are much greater than the previous value 2.4 Å^2 [4]. For sets V and VI, the maximum values of photodissociation cross section are much greater than the previous value [4]. The values of the maximum dissociation cross section depends on the nature of the potential-energy curves used and their relative positions. By comparing the results of sets III and IV, we find that the maximum cross section and the corresponding photon energy depends on the choice of the excited state curves. Comparing results of sets I and III, and those for sets II and IV we find that the result also depends on the nature of the ground-state potential. This is because of the fact that one of the factors that can affect the magnitude of the dissociation cross section is the overlap between the nuclear wave functions of the ground state and the excited state, together with the dipole transition moments (its dependence on the internuclear separation). The values of overlap may decrease if the excited state is shifted horizontally towards right with respect to the ground state. For set V and set VI we got almost identical results, since we have used almost the same set of curves. For all these calculations, we find that the difference in the threshold energy results in a shift in the spectrum and hence the position of maximum cross section is shifted as shown in Fig. 1. Comparing column 3 and column 5 of Table I, 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 the six sets of calculations and the difference is within a range of 10–159 cm^{-1}. Subtracting the energy in column 4 from that in column 3 of Table II, 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.

TABLE II. Zero-point energy for the ground state of NaH and the energy difference of the excited state from the two turning points of the ground vibrational level of the ground state.

Set	Energy diff. of $v''=0$ from r_e (cm^{-1})	Energy diff. at r_{min}(cm^{-1})(r_{min} in a.u.)	Energy diff. at r_{max}(cm^{-1})(r_{max} in a.u.)
I	543	35 520 (3.32)	32 338 (3.99)
II	579	35 813 (3.25)	32 727 (3.91)
III	567	36 260 (3.27)	33 224 (3.92)
IV	567	36 120 (3.27)	33 135 (3.92)
V	543	37 863 (3.32)	34 740 (3.99)
VI	543	37 865 (3.32)	34 742 (3.99)

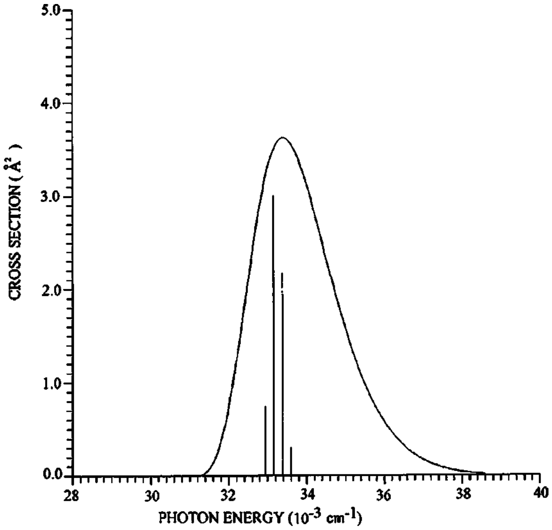

FIG. 2. Photodissociation spectrum using both the potential-energy curves from Sachs, Hinze, and Sabelli (set I). Franck-Condon factors multiplied by 6.2866 are shown by vertical lines. Franck-Condon values less than 0.1 have not been shown here.

We find that the energy of the ground vibrational level from the equilibrium-internuclear separation is different in each set (column 2 of Table II). This is because of the fact that the shape of the ground-state curve as well as the equilibrium separation for these curves is slightly different from each other. For set V, shift in the ground-state asymptote has

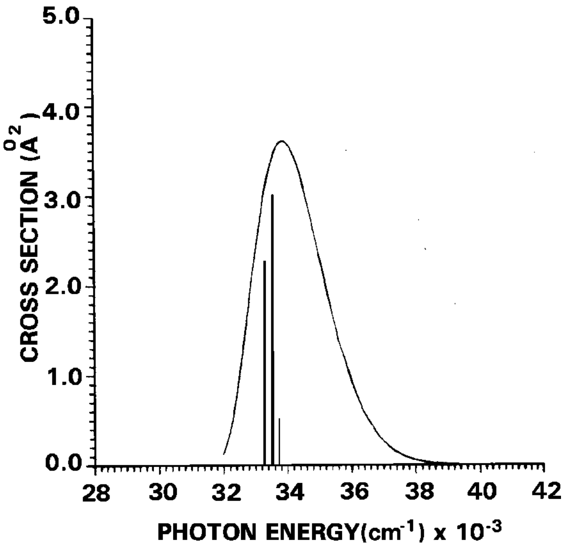

FIG. 3. Photodissociation spectrum using both the potential curves from Olson and Liu (set II). Franck-Condon factors multiplied by 5.89 have been shown by vertical lines. Franck-Condon factors less than 0.1 have not been shown.

negligible effect on the position of the ground vibrational level, from the minimum of the potential-energy curve.

In Figs. 2 and 3, we have shown the spectrum for set I and set II, respectively, alongwith the Franck-Condon factors around the maximum of the cross section. We find that the maximum of the Franck-Condon factor is very close to the maximum of the cross section obtained in these calculations. Therefore, one can conclude that the maximum photodissociation occurs mainly due to the Franck-Condon transitions.

We have presented here the results of six sets of calculations to show the dependence of the maximum photodissociation cross section and the corresponding photon energy on the choice of the potential-energy curves (original and rearranged). But out of these, we recommend that the results of set I can be used for further references. This is because of the fact that (i) in set I we have used the potential-energy curves and the corresponding dipole transition moments obtained from the same MCSCF calculations by Sachs, Hinze, and Sabelli and hence this calculation can be considered to be more consistent than others (sets II, III, and IV) and (ii) the ground state curve of Sachs, Hinze, and Sabelli is accurate enough to reproduce the experimental values [11] for the ratio of $R(J)$ and $P(J)$ transitions ($X\,^1\Sigma \rightarrow A\,^1\Sigma$) in NaH. Although the dissociation energy for the ground state and the dissociation threshold for the $B\,^1\Pi$ state obtained from Olson and Liu are closer to the lower limit of the experimental values [12] than those of Sachs, Hinze, and Sabelli the dipole transition moments for the $X\,^1\Sigma$ to $B\,^1\Pi$ transition have not been provided by them. Hence the results of the calculation (set II) with the potential energy curves of Olson and Liu cannot be recommended. We have shown here results of calculations with rearranged curves of Sachs, Hinze, and Sabelli to compare the values of photodissociation cross section and the photon energy for the maximum cross section with those of Kirby and Dalgarno (who also rearranged the curves of Sachs, Hinze, and Sabelli) and found that the results are significantly different. Therefore, we do not recommend calculations with rearranged curves since in that case the results will depend on the way the curves are rearranged. Nevertheless, more accurate calculations of potential-energy curves and dipole transition moments for NaH are needed, which can give more accurate dissociation energy for the ground state and the correct photodissociation threshold for the $B\,^1\Pi$ state.

V. CONCLUSIONS

We obtained photodissociation cross section of NaH using different potential-energy curves [1–3] for the ground $X\,^1\Sigma^+$ state and the excited state $B\,^1\Pi$. We have shown that the magnitude of the photodissociation cross section and the corresponding values of the photon energy depend on the choice of potential-energy curves. We have found that our results are significantly different from those obtained by Kirby and Dalgarno [4].

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