

FRANCK-CONDON FACTORS FOR THE  
CH<sup>+</sup> A<sup>1</sup>Π-X<sup>1</sup>Σ<sup>+</sup> TRANSITION\*

S. GREEN†

Goddard Institute for Space Studies, New York

AND

S. HORNSTEIN‡ AND C. F. BENDER

University of California Lawrence Livermore Laboratory

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## ABSTRACT

Accurate ab initio potential energy curves were used to calculate the vibrational eigenvalues and eigenfunctions for the A<sup>1</sup>Π and X<sup>1</sup>Σ<sup>+</sup> electronic states of CH<sup>+</sup>. The calculated Franck-Condon factors are  $q(0, 0) = 0.665$  and  $q(1, 0) = 0.249$ . These are in moderately good agreement with earlier values based on Morse potentials, but they differ markedly from recent values based on Rydberg-Klein-Rees potentials.

*Subject headings:* molecules — transition probabilities

## I. INTRODUCTION

The A<sup>1</sup>Π-X<sup>1</sup>Σ<sup>+</sup> transition of CH<sup>+</sup> is observed in interstellar absorption. As pointed out by Frisch (1972), knowledge of the electronic oscillator strength and vibrational Franck-Condon factors is necessary to convert the absorption data into optical depths and column densities; in particular, she noted the strong dependence of these quantities on the ratio of Franck-Condon factors  $q(0, 0)/q(1, 0)$ . The values in current use are  $q(0, 0) = 0.538$  and  $q(1, 0) = 0.287$ , which are given by Herbig (1968) based on Morse potential curves. Recently, Liszt and Smith (1972*a*) have given quite different values,  $q(0, 0) = 0.92$  and  $q(1, 0) = 0.06$ , based on Rydberg-Klein-Rees (RDR) potentials computed from the experimental vibrational data. Laboratory measurements have been made on transitions between the  $v'' = 0, 1$  vibrational levels of the lower and  $v' = 0, 1, 2, 3$ , and 4 levels of the upper state (Douglas and Morton 1960). The upper state is apparently shallow and very anharmonic; the vibrational energies are poorly represented by the usual power series in  $(v + \frac{1}{2})$ . This is not too surprising since the isoelectronic BH A<sup>1</sup>Π state is known to have a potential maximum (Johns, Grimm, and Porter 1967; Harrison and Allen 1969). Because of the unusual shape of the upper-state potential curve and the paucity of vibrational data for the lower state, one might seriously question the validity of Franck-Condon factors calculated from either Morse or RKR potentials. We hope to shed some light on this problem by calculating Franck-Condon factors from accurate ab initio potential energy curves.

## II. CALCULATIONS

The Green *et al.* (1972) ab initio curves used for this study were determined by approximating the eigenvalues (energy) and corresponding eigenvector (wave function)

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† National Research Council Resident Research Associate supported by the National Aeronautics and Space Administration.

‡ Visiting student; permanent address: Department of Chemistry, University of California, Berkeley, California.

TABLE 1  
ENERGY OF VIBRATIONAL LEVELS\*

| $v$    | $X \ ^1\Sigma^+$ | $A \ ^1\Pi$ |
|--------|------------------|-------------|
| 0..... | -31 756          | -7 738      |
| 1..... | -29 034          | -6 053      |
| 2..... | -26 437          | -4 618      |
| 3..... | -23 955          | -3 534      |
| 4..... | -21 585          | -2 728      |

\* In  $\text{cm}^{-1}$ . The zero of energy is taken at the separated atom limit.

TABLE 2  
FRANCK-CONDON FACTORS

| $A \ ^1\Pi$<br>$v'/v''$ | $X \ ^1\Sigma^+, v/v''$ |       |       |       |       |
|-------------------------|-------------------------|-------|-------|-------|-------|
|                         | 0                       | 1     | 2     | 3     | 4     |
| 0.....                  | 0.665                   | 0.262 | 0.062 | 0.009 | 0.001 |
| 1.....                  | 0.249                   | 0.175 | 0.334 | 0.178 | 0.051 |
| 2.....                  | 0.062                   | 0.259 | 0.000 | 0.167 | 0.256 |
| 3.....                  | 0.015                   | 0.139 | 0.068 | 0.098 | 0.000 |
| 4.....                  | 0.005                   | 0.071 | 0.100 | 0.012 | 0.055 |

of the nonrelativistic Born-Oppenheimer Hamiltonian, using a configuration interaction approach. This technique, the most accurate available today, has yielded dissociation energies to within 0.1 eV and one-electron operator properties to within 0.1 percent. The reader is referred to Schaefer (1972) for discussions of the accuracy of such calculations and to Green *et al.* (1972) for details of the  $\text{CH}^+$  work. The accuracy of the  $\text{CH}^+$  results may be inferred by comparing the following calculated properties with the experimental values (in parentheses): equilibrium internuclear distances  $R_e(X) = 1.130$  (1.131) Å and  $R_e(A) = 1.234$  (1.234) Å;  $X$  to  $A$  transition energy  $T_e = 24551$  (24145)  $\text{cm}^{-1}$ ; and dissociation energy  $D_0^o(X) = 4.04$  (3.94) eV.

Continuous potential curves were approximated using a cubic spline program developed by Young (1967). The vibrational eigenfunctions and eigenvalues were calculated by direct numerical integration of the one-dimensional Schrödinger equation. For further details of this procedure see Blatt (1967). To guarantee numerical stability, more than 800 equally spaced points were used for the numerical integration. The vibrational levels for both states are given in table 1. The energy spacing between the two ground vibrational states is calculated to be  $\nu_{00} = 23597 \text{ cm}^{-1}$ .

Finally, the Franck-Condon factors were evaluated by numerically integrating the tabulated wave functions. The factors are given in table 2. Notice that the vibrational sum rule (see Herzberg 1950) holds well for the first two vibrational levels of both the  $X$  and  $A$  states.

### III. DISCUSSION

The RKR method is normally considered definitive for generating experimental potential energy curves. (See, for example, Fallon, Vanderslice, and Mason 1960 and Zare 1964 and references therein.) However, for RKR to work properly, the energy must be expressible as a reasonably well behaved function of continuous vibration-rotation quantum numbers (continuous in the classical sense). This is normally achiev-

ed through the spectroscopic power-series expansions in  $(v + \frac{1}{2})$ . This will not be possible if the potential has a very unusual shape or if there are insufficient spectroscopic data. It is for such cases that a quantum-mechanical potential would be most useful if it could be computed with enough accuracy. As noted previously, the calculated CH<sup>+</sup> curves have a relative accuracy of about 0.1 eV in going from molecule to separated atoms and from one electronic state to another. While this is generally adequate for chemical accuracy (1 eV = 23.1 kcal per mole), it is orders of magnitude poorer than normal spectroscopic accuracy (1 eV = 8065.7 cm<sup>-1</sup>). It is reasonable to suppose, however, that these curves are relatively more accurate for the small variations in internuclear distance near  $R_e$  which are important in the lower vibrational states. Indeed, a good test of the shape of the computed potentials near their minimum is provided by comparing the calculated and experimental vibrational energy spacing. For the ground state the calculated (and experimental) values, in cm<sup>-1</sup>, are  $\Delta G(1/2) = 2722$  (2739.7); for the upper state  $\Delta G(1/2) = 1685$  (1642.2),  $\Delta G(3/2) = 1435$  (1434.2), and  $\Delta G(5/2) = 1084$  (1242.0). This agreement is quite encouraging and leads us to believe that Franck-Condon factors may indeed be reliably computed from ab initio potentials, at least for the lower vibrational levels.

Because of the large discrepancy between our Franck-Condon factors and those reported by Liszt and Smith (1972a) we have recomputed the RKR potential for the upper state in order to compare it with our ab initio curve. Using the computer program of Zare and the spectroscopic data of Douglas and Morton (1960), we obtained turning points in excellent agreement with the CI potential. Furthermore, using the RKR curve for the upper state and the ab initio curve for the lower state, we obtained Franck-Condon factors in agreement with those given in table 2. The CI curves for both states are expected to be of comparable accuracy; the RKR curve for the lower state, however, may be significantly poorer than that for the upper state. We, therefore, believe that the Franck-Condon factors presented here are significantly more reliable than those previously reported. Since this study was completed, Liszt and Smith (1972b) have noted an error in the RKR analysis. Their revised Franck-Condon factors are now in good agreement with those calculated from the ab initio curves.

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## EDITORIAL

### I. SUBJECT INDEXING

Starting with the recent January 1 issue, each paper in the *Journal* will have attached to it (immediately below the abstract) the appropriate subject headings that will be used in compiling analytical annual, and five-year subject indexes. The initial selections of headings are made by the Managing and Letters Editors from a master list currently having more than 200 entries. Authors are then invited to make deletions or additions that they think are appropriate from furnished copies of the master list. We trust that this system will allow faster and easier recovery of information in the *Journal*.

### II. PLANOGRAPHING PAGE CHARGES

By action of the Council of the American Astronomical Society, the page charge for planographed material has been lowered from the previous \$15 to the current \$10 per page for all parts of the *Journal*, effective 1973 January 1. This reduction is the result of a more realistic assessment of the costs involved. We hope that the reduction will encourage the publication, particularly in the Supplement Series, of basic observational data and computational results.

We should reiterate that computer printout is accepted only reluctantly by the *Journal* because of its poor legibility. Authors are encouraged to arrange for the best possible printout (using new ribbons and unbroken keys) or for the transcription to typed pages.

### III. COLOR REPRODUCTIONS

Occasionally color reproductions are desired to illustrate features in astronomical photographs or to add an additional dimension in portraying graphical material. The *Journal* is now prepared to print color reproductions, although the cost is very high and the process is not likely to be used frequently. If the authors furnish the color-separation negatives and progressive color proofs, the page charge will be \$900 for the first page and \$60 for each additional pages, up to a total of 12 pages per issue. If the *Journal* is to provide the negatives, the corresponding costs are \$1200 and \$130, respectively.

### IV. NEW COMPOSITORS

Because of increased costs, the *Journal* is no longer having its composition done by the University of Chicago Printing Department (although the University of Chicago Press will continue to publish the *Journal*). Starting with the recent 1972 October 1 issue, composition for Part 1 has been done by William Clowes & Sons, Ltd., London, England, and for Part 2 by Heffernan Press, Worcester, Massachusetts. The printing of the *Journal* will continue to be done, as it has been in recent years, by Segerdahl-Halford Printing Co., Inc., Chicago, Illinois. We anticipate that the quality of the *Journal* typography will, after initial irregularities and exploration of techniques, be of the same high quality as before and that the 20 percent saving in costs will help forestall price increases. We request the patience of authors and readers during the transition. For instance, for the recent October 1–December 1 issues the authors saw

first-run galley proofs, rather than second-run proofs as under the previous system and eventually under the new one. First-run galleys have many more obvious errors, although the final product received the same careful editorial treatment.

HELMUT A. ABT  
*Managing Editor*

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