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Effect of electron correlation on the H_2CO-He interaction potential

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A previously reported Hartree-Fock (HF) interaction potential between $H_2CO(^1A_1)$ and $He(^1S)$ is modified through a series of configuration interaction (CI) calculations. The CI contribution is described by a three-term ($l = 0,1,2$) Legendre polynomial expansion in the angle θ formed by the direction of incidence of He and the CO bond of formaldehyde. No significant azimuthal angle dependence is obtained. Correlation is found to have little effect in the strongly anisotropic repulsive region of the interaction potential but dominates the well and long-range regions. The maximum well depth is attained for in-plane approaches of He and lies in the range 35–40°K for arbitrary θ at center of mass separation of 7.5 a.u. The CI contribution in the region of the minimum is believed accurate to ~20%.

I. INTRODUCTION

In a previous paper, we reported a Hartree–Fock (HF) interaction potential for the $H_2CO(^1A_1)$–$He(^1S)$ system.[1] It is known that the HF method describes only the average interaction between electrons of colliding molecules. Hence for neutral–neutral interactions, the HF method cannot provide an accurate description of the interaction energy in regions where the dispersion interaction plays an important role, since the dispersion interaction arises from the instantaneous mutual response of one molecule to another.[2] Therefore, a correlated calculation is required to yield this contribution to the interaction energy.[2,3] Because accurate scattering cross sections at very low energies are sought for the H_2CO–He system,[4] it is important to determine the correlation correction to the HF potential.[5]

It is useful to divide the H_2CO–He interaction potential into three parts, a highly anisotropic repulsive region at small internuclear separations, a region containing the energy minimum at intermediate distances, and a long-range region. The dominating forces in these regions have different physical origins which dictate the use of selected methods for each. Since electron correlation is only a small fraction of the interaction energy at short range (where closed-shell repulsive forces dominate), the potential energy surface in this region is believed to be well described by our previous HF results. In the nonoverlap region, perturbation theory estimates show that the dispersion interaction is dominant and that induction contributions (obtainable in the HF approximation) are negligible. Little is known *a priori* about the region near the minimum. Since the HF well depth is quite small (~3°K), it is clear that the CI contribution will significantly alter the potential in this region. Therefore CI calculations are needed to complete the interaction potential for the H_2CO–He system.

Since only small van der Waals attractions arise from dispersion forces, special care must be given to the type of CI calculation performed. Of course, one would like to determine the correlation contribution to the interaction energy from a full CI calculation but that is at present economically unfeasible for most systems. Extensive work on the He_2 system,[6–8] which similarly has a small van der Waals minimum, guides our approach to this problem. By carefully choosing configurations for the He_2 system, the dispersion energy was calculated directly (Di-CI).[6,8] The main advantage of this method is that the error owing to lack of completeness of the basis set (superposition error) is eliminated.[8] However, it does not take into account change in intramolecular correlation of each molecule with internuclear distance.[7,8] Since the change in intramolecular correlation increases with decreasing intermolecular distance, this method overestimates the well depth. As shown by Liu and McLean,[8] the intermolecular and the intramolecular correlations are *not* additive, thus one cannot add the dispersion energy and the intramolecular correlation to obtain the total CI contribution. To include intramolecular correlation, a CI calculation may be performed which includes all single and double excitations from the HF reference state (S + D CI). Such a computation approximates the total CI energy including dispersion and intramolecular correlation energy. It also includes the superposition error, however, which generally leads to an artificial increase in well depth. For He_2 a full CI was carried out yielding a well depth of −10.7°K[8b] that is bracketed by the Di-CI value (−12.1°K)[8a] and the S + D CI limit result (−9.3°K).[8a] Unfortunately, as of this writing, there is no basis upon which to presume that this bracketing will hold rigorously for other systems. However, it does show that interaction energies obtained by the various methods are

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TABLE I. Correlation energies ($E_{CI}-E_{HF}$) for H_2CO–He.[a]

R(a.u.)	θ / φ	0° / 0°	90° / 0°	90° / 90°	180° / 0°
5		−0.000891	−0.000737	−0.000709	−0.002247
		−281.4	−232.7	−223.9	−709.6
7		−0.000171	···	···	−0.000294
		−54.0	···	···	−92.8
8		−0.000064	−0.000040	−0.000026	−0.000115
		−20.2	−12.6	−8.2	−36.3
		(−22.9)[b]			(−41.9)
11		−0.000005	−0.000001	−0.000001	−0.000009
		−1.6	−0.3	−0.3	−2.8
		(−2.9)			(−4.9)

[a]Order of entries in the table: energy in a.u. and °K, where 1 °K = 3.1668×10^{-6} a.u..
[b]Energies (°K) in parenthesis are from the Di-CI calculation.

roughly equal. For the larger H_2CO–He system, it was economically feasible to perform only Di-CI and S + D CI calculations.

Section II describes the calculations, Sec. III discusses the results, and Sec. IV summarizes the findings of the paper.

II. DESCRIPTION OF CALCULATION

In the present study, H_2CO is assumed to be a rigid rotor with the same geometry as used for the HF surface.[1] The coordinates of He are R, the intermolecular distance from the H_2CO center of mass, θ, the polar angle from the CO bond, and φ, the azimuthal angle measured from the plane of the molecule.

To obtain the CI energy, we initially chose to calculate the dispersion energy by the following procedure (Di-CI): (a) compute the HF energy of the system, (b) localize the occupied orbitals,[9] (c) generate configurations that include single and double excitations corresponding to removal of one electron from a H_2CO orbital and one electron from the He orbital, and (d) place the excited electrons into all possible spin and symmetry allowed combinations of HF virtual orbitals.[10] (In all Di-CI calculations the two lowest orbitals, which correspond to O and C 1 s cores, are frozen, i.e., no excitations are permitted.) By calculating the dispersion energy in this manner, no superposition error arises. Using this method at $R = 8$ and 11 a.u. for both $\theta = 0°$ (O-atom end) and 180° (C-atom end) yields an interaction at the C-atom end that is twice as attractive as that at the O-atom end (see Table I). This finding is contrary to what one would expect from HF results[1] where, for fixed R, the interaction at the C-atom end was more repulsive than that at the O-atom end. To verify these values, S + D CI calculations were performed[11] at the same geometries, again holding the lowest two orbitals fixed. The S + D CI interaction energies were in close accord with Di-CI values. As in the He_2 study,[8] the Di-CI procedure yields a larger well depth than the S + D CI method.

In the HF H_2CO–He study, a very large basis set (basis B) was used to reduce the superposition error.[1] Since the expense of using basis B for the two types of CI calculations described above is presently prohibitive, basis A was reexamined. At $R = 8$ a.u. and $\theta = 0°$, the superposition error is at most 7 °K. Since Di-CI and S + D CI computations are in reasonable agreement using basis A, we feel that the superposition error is likely not larger than 7 °K for the geometries considered here. For these reasons, it is felt that basis set A should provide an adequate description of the well and long-range regions and therefore is used for the remainder of the calculations.

Although the Di-CI and S + D CI methods yield comparable results, the available S + D CI computer code is faster and therefore was the one used for the bulk of the calculations. CI computations were performed at 14 geometries: $\theta = 0°$ and 180° for $R = 5, 7, 8,$ and 11 a.u.; $\theta = 90°$, $\varphi = 0°$ (plane of H_2CO) for $R = 5, 8,$ and 11 a.u.; and $\theta = 90°$, $\varphi = 90°$ (bisector plane) for $R = 5, 8,$ and 11 a.u.. The number of configurations included in the CI wavefunctions depends, of course, on the molecular point group. As discussed elsewhere,[12] each configuration is a pure spin eigenfunction with $S = 0$. The geometries $\theta = 0°$ and 180° correspond to C_{2v} symmetry (19 452 configurations in the S + D CI), $\theta = 90°$, $\varphi = 0°$ corresponds to C_s symmetry (37 779 configurations), and $\theta = 90°$, $\varphi = 90°$ also corresponds to C_s symmetry (34 419 configurations), but a different plane of symmetry is involved:

III. RESULTS AND DISCUSSION

Correlation energies are given in Table I. These values do not include the HF interaction energy and thus must be added to the HF results to get the complete interaction potential. Because of the limited information available for $\theta = 90°$, no correlation contribution to the φ dependence can be ascertained.

To facilitate the use of the energy surface in scattering calculations, the correlation contribution is expanded in spherical harmonics. Following Ref. 1, the angular dependence of the correlation contribution is expressed in the form

$$V(R,\theta) = v_{00}(R) + v_{10}(R)\cos\theta + \tfrac{1}{2}v_{20}(R)(3\cos^2\theta - 1)\ . \quad (1)$$

Inverting Eq. (1) gives

$$v_{00}(R) = [V(R,0°) + V(R,180°) + 4V(R,90°)]/6\ , \quad (2)$$

$$v_{10}(R) = [V(R,0°) - V(R,180°)]/2\ , \quad (3)$$

and

$$v_{20}(R) = [V(R,0°) + V(R,180°) - 2V(R,90°)]/3\ . \quad (4)$$

From Eq. (1)–(4), the correlation contribution can be interpolated for all desired values of R and θ.

Contour plots of the HF and CI interaction energies in the plane of the $H_2CO(\varphi = 0°)$ and the bisector plane ($\varphi = 90°$) are given in Fig. 1. As expected, the strongly repulsive region is virtually unchanged by including electron correlation. The correlation contribution increases the well depth from 3 °K in the HF surface to 35–40 °K and shifts the minimum inward from 9 to 7.5 a.u..

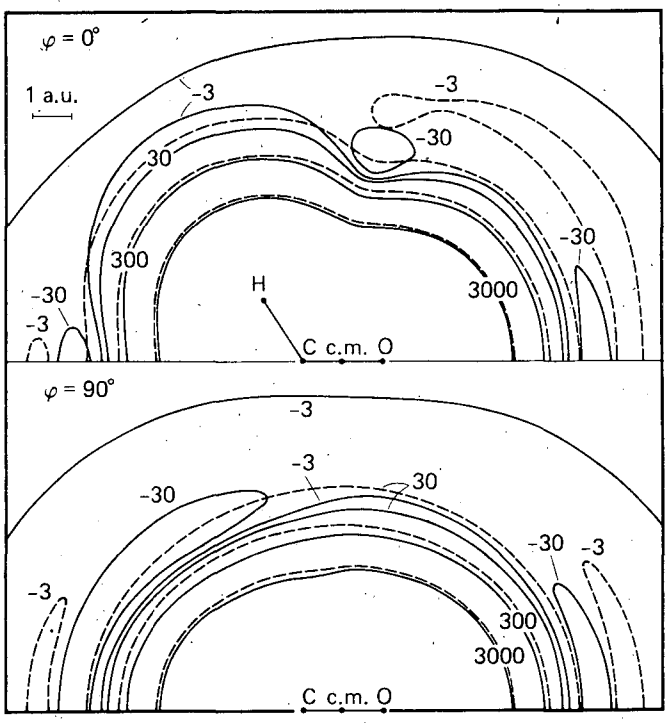

FIG. 1. Contour plots of the interaction potential for He incident in the plane of $H_2CO(\varphi = 0°)$ and He incident in the bisector plane ($\varphi = 90°$). ——CI interaction potential. - - - HF interaction potential. Energies in °K. c.m. denotes center of mass.

Based on the close agreement of the Di-CI and S+DCI calculations in the well region (R = 8 a.u.), the final CI interaction energies are believed reliable to ~ 20%.

IV. SUMMARY

A CI calculation has been performed to ascertain the role of electron correlation on the interaction potential between a rigid formaldehyde molecule and a helium atom. Efforts were concentrated on the region of the energy minimum and at large intermolecular distances where correlation effects are expected to have their largest effect.

Two types of CI calculations were carried out. In one method (Di-CI), the dispersion energy was calculated directly by judicious selection of configurations. In the second procedure (S+D CI), the interaction energy was determined from a CI wavefunction built from inclusion of all single and double excitations from a HF reference state. Interaction energies obtained by the two procedures were in reasonable agreement. It is noted that the Di-CI method yields a somewhat larger well depth than the S+D CI procedure as anticipated from previous He_2 studies.[8] CI interaction energies in the vicinity of the minimum have an estimated uncertainty of 20%.

To facilitate scattering studies, the CI interaction energies were fit to a spherical harmonic expansion. Three terms were used to describe the θ dependence; no significant out-of-(H_2CO) plane dependence φ was obtained. The effect of correlation on the well region is to deepen the well from ~ 3 °K to 35–40 °K and to shift the minimum inward from a H_2CO–He center of mass separation of 9 to 7.5 a.u..

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[10]The Joint MOLECULE-ALCHEMY program package incorporates the MOLECULE integral program and the ALCHEMY-SCF program. MOLECULE was written by Dr. J. Almlöf of the University of Uppsala, Sweden. The ALCHEMY-SCF program was written by Drs. P. S. Bagus and B. Liu of the IBM San Jose Research Laboratory. The interfacing of these programs was performed by Drs. U. Wahlgren (presently at the University of Uppsala) and P. S. Bagus at IBM. For a description of MOLECULE see J. Almlöf, "Proceedings of the Second Seminar of Computational Problems in Quantum Chemistry," p. 14, Strassburg, 1972 (Max-Planck Institute, Munich 1973). For a description of the ALCHEMY-SCF program, see: P. S. Bagus, "Documentation for ALCHEMY-Energy Expressions for Open Shell Systems," IBM Research Report RJ 1077 (1972). The ALCHEMY quantum chemistry programs were written primarily by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine of the Theoretical Chemistry Group at IBM Research in San Jose, California. Preliminary descriptions of the program are given in: (a) A.

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