INTERACTION POTENTIAL BETWEEN FORMALDEHYDE AND HELIUM

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I. Introduction

In 1969 Palmer et al.[1] reported absorption of the isotropic radiation of 4830 MHz by the $1_{10} \leftarrow 1_{11}$ transition of H_2CO in cool dust clouds in our galaxy. Since that observation, this transition has been seen against many galactic continuum sources and the 2.7°K cosmic background radiation at 6 cm. wavelength.[2] The latter absorption is anomalous because it implies that the excitation temperature characterizing the populations in the 1_{11} and 1_{10} levels, the lowest doublet of ortho formaldehyde, is lower than both the isotropic background radiation temperature and the expected kinetic temperature. To obtain such an excess population in the lower 1_{11} state requires a nonthermal excitation mechanism.

The mechanisms proposed to account for the anomalous absorption involve collisional or radiative excitation to higher rotational states of H_2CO and subsequent radiative decay predominantly to the 1_{11} state. Evans et al.[2] have recently given a convincing discussion indicating that a collisional pump is the only model that accounts for all of the observations and satisfies necessary criteria.

To test the collision hypothesis requires calculation of cross sections for rotational excitation of H_2CO by likely scatterers H_2 and He, followed by solution of the equations of statistical equilibrium[3] employing the computed cross sections. The solution of the equations of statistical equilibrium yield excitation temperatures as a function of density of scatterer for specified kinetic temperatures.

Although solving the equations of statistical equilibrium is a straightforward procedure, the validity of the final results rests on the accuracy of the cross sections used. Furthermore, the reliability of the computed cross sections depends both on the rigor of the formulation followed in the dynamics calculation and the accuracy of the intermolecular potential used in the determination of scattering cross sections. It is the first step, determination of the interaction potential, which is briefly described in the remainder of the present paper.

II. Determination of Interaction Potential and Discussion

In the present study, helium is chosen as the collision partner because of the fewer degrees of freedom that must be treated compared to H_2. It is likely that the conclusions of a complete dynamics treatment using He would not seriously differ from results employing H_2.

Unlike earlier studies of the anomalous absorption problem in H_2CO,[4] a rigorous quantum-mechanical approach is followed here. Hartree-Fock (HF)[5] calculations were carried out following the Roothaan approach[6] with H_2CO constrained to the equilibrium geometry of $R_{CO} = 1.208\text{Å}$, $R_{CH} = 1.116\text{Å}$, and $< HCH = 116°31'$ reported by Takagi and Oka.[7]

An extended expansion set was used in the HF calculation which included at least three basis functions per valence electron on each atom plus functions to describe the induction (polarization) effect of one scatterer on the other. It is known, however, that the HF approximation describes only the average motion of electrons of a system and therefore cannot describe the dispersion interaction. Recall that the dispersion interaction arises from the instantaneous motion of molecular electrons so that a correlated approach is necessary for its determination. Because kinetic energies in the interstellar medium are low ($\lesssim 100°$) and of the same order of magnitude as attractive induction and dispersion interactions in the present system, it is essential to ascertain the correlation contribution to the interaction energy.[8]

To achieve this end, configuration interaction (CI) calculations were carried out for a limited range of geometries in the region of the HF potential minimum and at long range. Figure 1 summarizes the results of the HF and CI calculations. Correlation is seen to be crucial for an accurate description of the H_2CO - He interaction potential. Quantum-mechanical calculations of rotational excitation cross sections are nearing completion using the CI potential. These studies are the first ab initio treatment of both intermolecular potential and dynamics for the interaction of a polyatomic molecule with an atom.

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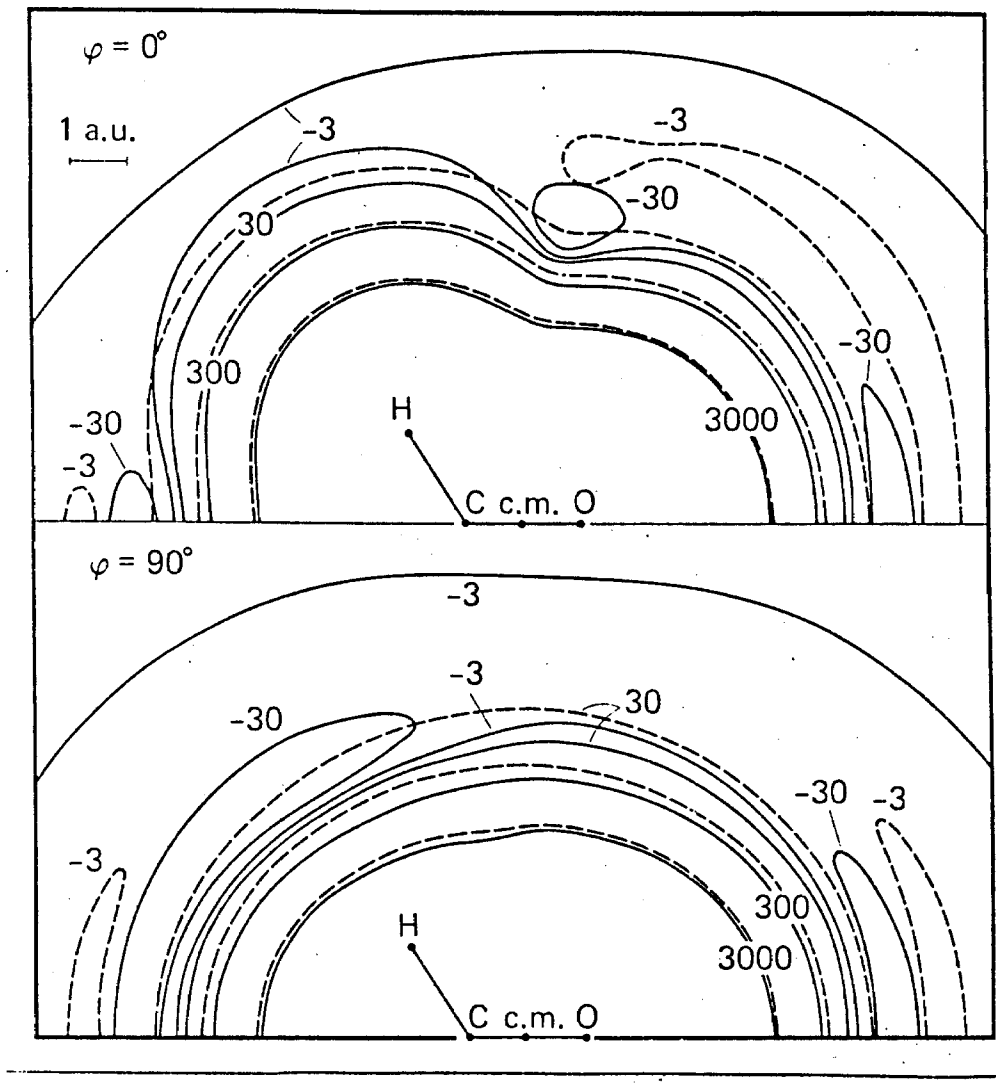

Figure 1. Contour plots of the interaction potential for He incident in the plane of H_2CO ($\varphi = 0°$) and He incident in the bisector plane ($\Phi = 90°$). ——— CI interaction potential. — — — HF interaction potential. Energy in °K. c.m. denotes center of mass.

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