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CLASSICAL TRAJECTORY STUDY OF ROTATIONAL EXCITATION IN LOW ENERGY He - CO AND He - H_2 COLLISIONS*

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ABSTRACT

Classical trajectory calculations for the rotational excitation of CO and H_2 by collision with He have been carried out and compared to the accurate quantum mechanical calculations of other workers. The agreement is reasonably encouraging, although some inherent limitations of this strictly classical approach are observed and discussed.

I. INTRODUCTION

Rotational excitation in molecular collision systems is typically a strong, or "classically allowed"[1] process, meaning simply that there exists classical trajectories along which the requisite amount of rotational excitation takes place. As a function of initial collision energy, for example, a rotational excitation cross section usually rises from zero sharply at its energetic threshold. This is in contrast to vibrationally inelastic transitions which are typically weak, "classically forbidden"[1] processes; it often requires collision energies significantly above the energetic threshold for these transitions to have a sizeable cross section.

The most important quantum effects in classically allowed processes are of an interference nature.[2] Often, however, the averaging over impact parameter, m-components of rotational states, etc., quench this interference structure so that a completely classical treatment becomes adequate. The rule of thumb, therefore, is that a completely classical treatment (eg. a quasi-classical trajectory calculation) is adequate to describe integral cross sections for inelastic collision processes that are classically allowed.

It is important to test the validity of the above "rule of thumb" by comparison of classical calculations with accurate quantum mechanical results whenever the latter are available. La Budde and Bernstein[3] have made such a comparison for the $0 \rightarrow 2$ rotational excitation of H_2 by collision with Li^+. Even though

only a few quantum states are involved in this process, they nevertheless find quite good agreement between their quasi-classical trajectory calculation[3] and the accurate coupled channel quantum mechanical calculations of Lester and Schaefer.[4]

Green and Thaddeus[5] have recently carried out accurate quantum mechanical coupled channel calculations for rotational excitation of CO by He, and this has motivated us to generate the classical trajectory results to provide another comparison of dynamically exact classical mechanics with dynamically exact quantum mechanics. To provide an even more stringent test of the classical approach we have carried out a similar calculation for the $0 \rightarrow 2$ rotational excitation of H_2 by He, comparing with Shafer and Gordon's[6] and Green's[7] accurate coupled channel calculations. The He - H_2 system should be the <u>weakest</u> rotational transition of any atom-diatom collision system and the one for which the purely classical treatment is thus most questionable.

II. METHODOLOGY

The He - CO and He - H_2 collision systems are both treated as rigid rotor-atom system, the potentials being the same as those used for the quantum calculations.[5,6] The classical calculations were carried out in a way which is equivalent to the now standard quasi-classical trajectory procedure.[8]

The rotational quantum number j is defined by

$$E_{rot} = B\ (j + \tfrac{1}{2})^2 \tag{2.1}$$

where E_{rot} is the classical rotational energy of the rotor and B the rotational constant (B_{H_2} = 60.99 cm^{-1}, B_{CO} = 1.9226 cm^{-1}). Trajectories were all begun with j = 0, and after collision the final rotational quantum number was determined by first solving for the final non-integral value of j from equation (2.1) and then assigning the closest integer (the closest <u>even</u> integer for H_2). The cross section for the $0 \rightarrow j$ transition is then given by

$$\sigma_{j\leftarrow 0} = \pi\ b_{max}^2\ (N_j/N_{tot}) \tag{2.2}$$

where b_{max} is the maximum impact parameter which defines the usual impact parameter sampling[8] (i.e., $b = b_{max}\sqrt{\xi}$, where ξ is a random number), N_{tot} is the total number of trajectories run, and N_j is the number of these for which the final rotational quantum number is j.

III. RESULTS

Figure 1 shows the results of the trajectory calculations for the $0 \rightarrow 2$ rotational excitation of H_2 by He, compared with the quantum mechanical results of Shafer and Gordon[6] and Green[7]; this comparison is entirely analogous to that made by La Budde and Bernstein[3] for $Li^+ + H_2$. The agreement of the classical and quantum results in Figure 1 is not as good as that for the $Li^+ + H_2$ case,[3] but this is expected since the cross section for He - H_2 is much smaller and for $Li^+ - H_2$. Given the fact that the He - H_2 system should be as weak a rotational excitation as for any molecular collision system, the agreement in Figure 1 is encouraging.

Cross sections for the $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, and $0 \rightarrow 4$ excitations of CO by He are shown in Figure 2 as a function of initial translational energy, along with the quantum mechanical results of Green and Thaddeus.[5] The overall agreement is quite reasonable, probably typical of what one should expect of a quasi-classical trajectory calculation.

A more interesting comparison, which reveals some of the inherent limitations of a purely classical theory, is shown in Figure 3; here the cross section for the $0 \rightarrow j$ excitation is plotted as a function of j for a fixed initial translational energy. (The comparison is similar for other values of E.) The quantum mechanical results[5] show an oscillatory structure which the classical values do not reproduce; this is the reason that the classical cross sections for the $0 \rightarrow 2$ and $0 \rightarrow 3$

transitions in Figure 2 are consistently too small and too large, respectively.

This interference effect seen in Figure 3 can be understood as the remnant of the $\Delta j = 2$ selection rule that would exist if CO were a homonuclear molecule; i.e., if CO were homonuclear the $0 \rightarrow j$ cross sections would be identically 0 for odd j, rather than simply diminished. This means that the P_2 term in the He - CO potential is somewhat stronger than the P_1 term. (For the homonuclear case P_1 term is completely absent.)

Classical S-matrix theory[1,2]--a semiclassical approach which uses classical trajectories but which also incorporates the superposition principle of quantum mechanics--is able to account for the $\Delta j = 2$ selection rule for the homonuclear case quite naturally: classical trajectories with odd Δj exist in the homonuclear case, but the addition of the appropriate amplitudes results in totally destructive interference and thus a net amplitude of zero for these transitions. For the "almost homonuclear" case there will still be this type of interference which diminishes--but does not completely annihilate--the odd Δj transitions. It is clear, therefore, that a classical S-matrix calculation would produce the interference structure seen in Figure 3; such a calculation, however, is more difficult to carry out than the present purely classical ones.

IV. CONCLUDING REMARKS

This paper has presented two more comparisons of exact classical and exact quantum mechanics for a three dimensional atom-diatom collision. The results tend to support the thesis that a purely classical approach is quite useful for describing inelastic collision processes that are classically allowed. It has also been noted that rotational excitation is almost always a classically allowed process, even for perhaps the weakest of all possible cases, the excitation of H_2 by He. Purely classical approaches cannot, of course, produce quantum interference effects, such as those seen in Figure 3; if it is necessary to describe these effects correctly, then a more sophisticated theory will be required, eg. a purely quantum treatment, or an approach such as classical S-matrix theory.

Finally, we have not addressed the question of which approach--coupled channel or classical trajectory--is easier computationally, i.e., takes less computer time. The quantum calculations become easier the lower the collision energy because fewer channels are required in the coupled channel expansion. The classical calculations, on the other hand, become easier with increasing energy because the trajectories run faster. (A typical He - CO trajectory took 1.0 and 0.4 seconds at an energy of 10 and 150 cm^{-1}, respectively, on a CDC 7600; a He - H_2 trajectory required 0.08 - 0.09 seconds for the entire energy range 600-5000 cm^{-1}.) At what energy the computational advantage switches from the quantum to the classical approach is not clear, and it will of course depend on the particular system

under study. The important point is that there seems to be a broad overlap of the regions for which the quantum and the classical calculations can both be carried out with reasonable effort and for which the classical treatment is moderately reliable.

ACKNOWLEDGMENT

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† Camille and Henry Dreyfus Teacher-Scholar.

1. For a more precise discussion of the terms "classically allowed" and "classically forbidden" in the sense that we use them, see for example, W. H. Miller, J. Chem. Phys. 53, 3578 (1970). See also ref. 2.
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FIGURE CAPTIONS

Figure 1. The cross section for the $0 \rightarrow 2$ rotational excitation of H_2 by He, as a function of initial translational energy. The solid curve shows the accurate quantum mechanical calculations of Shafer and Gordon[6] and Green,[7] and the dashed curve the classical trajectory results.

Figure 2. The cross section for the $0 \rightarrow j$, $j = 1 - 4$, rotational excitation of CO by He, as a function of initial translational energy. The solid curve is the accurate quantum mechanical result of Green and Thaddeus,[5] and the dashed curve the results of the classical trajectory calculation.

Figure 3. The same quantity as in Figure 2 (solid line = quantum, dashed line = classical) but shown as a function of final rotational quantum number j for a given initial translational energy $E = 100\ cm^{-1}$.

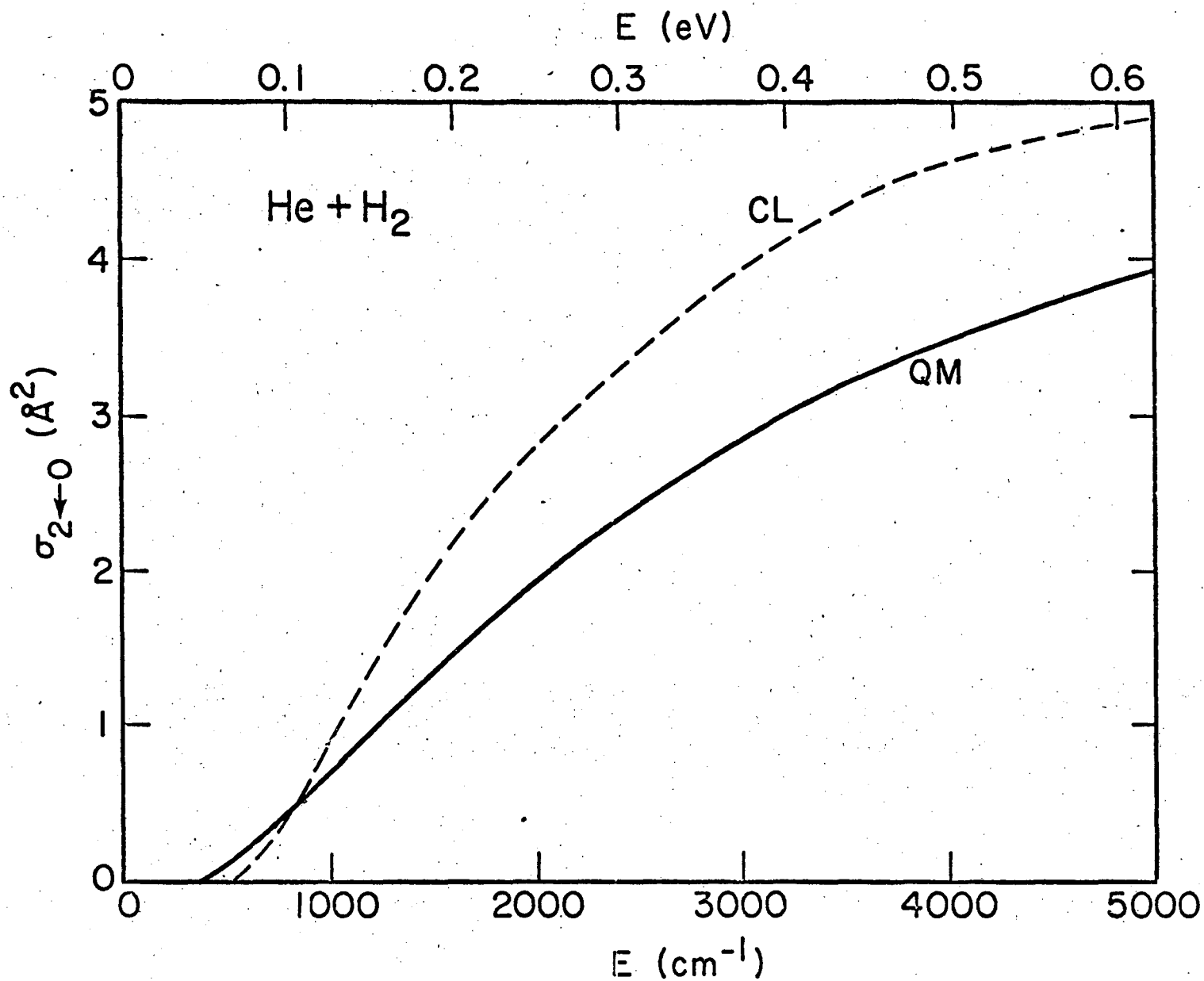
E (eV)
0
0.1
0.2
0.3
0.4
0.5
0.6
He + H2
CL
QM
σ2←0 (Å2)
5
4
3
2
1
0
0
1000
2000
3000
4000
5000
E (cm-1)

Fig. 1

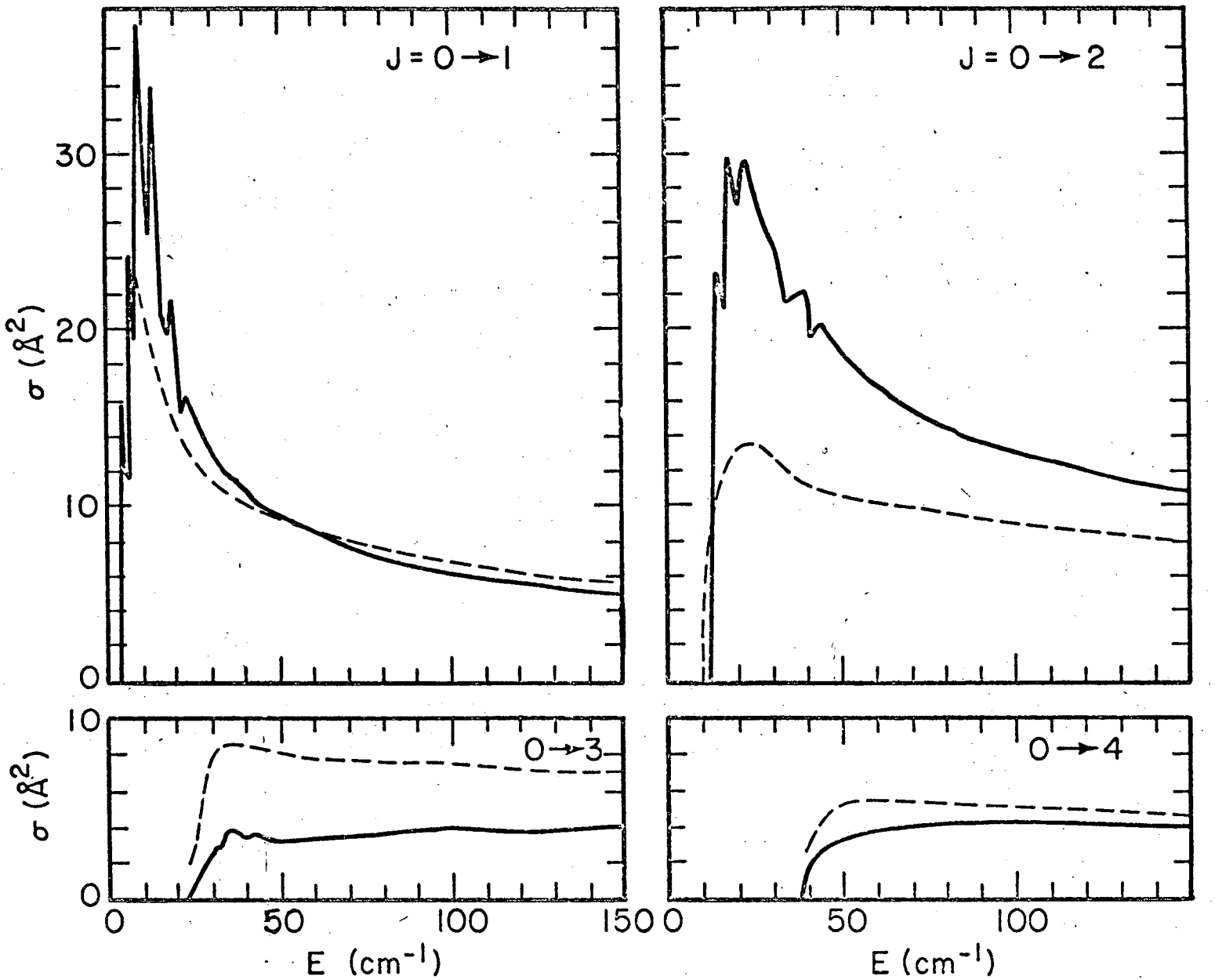

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Fig. 2

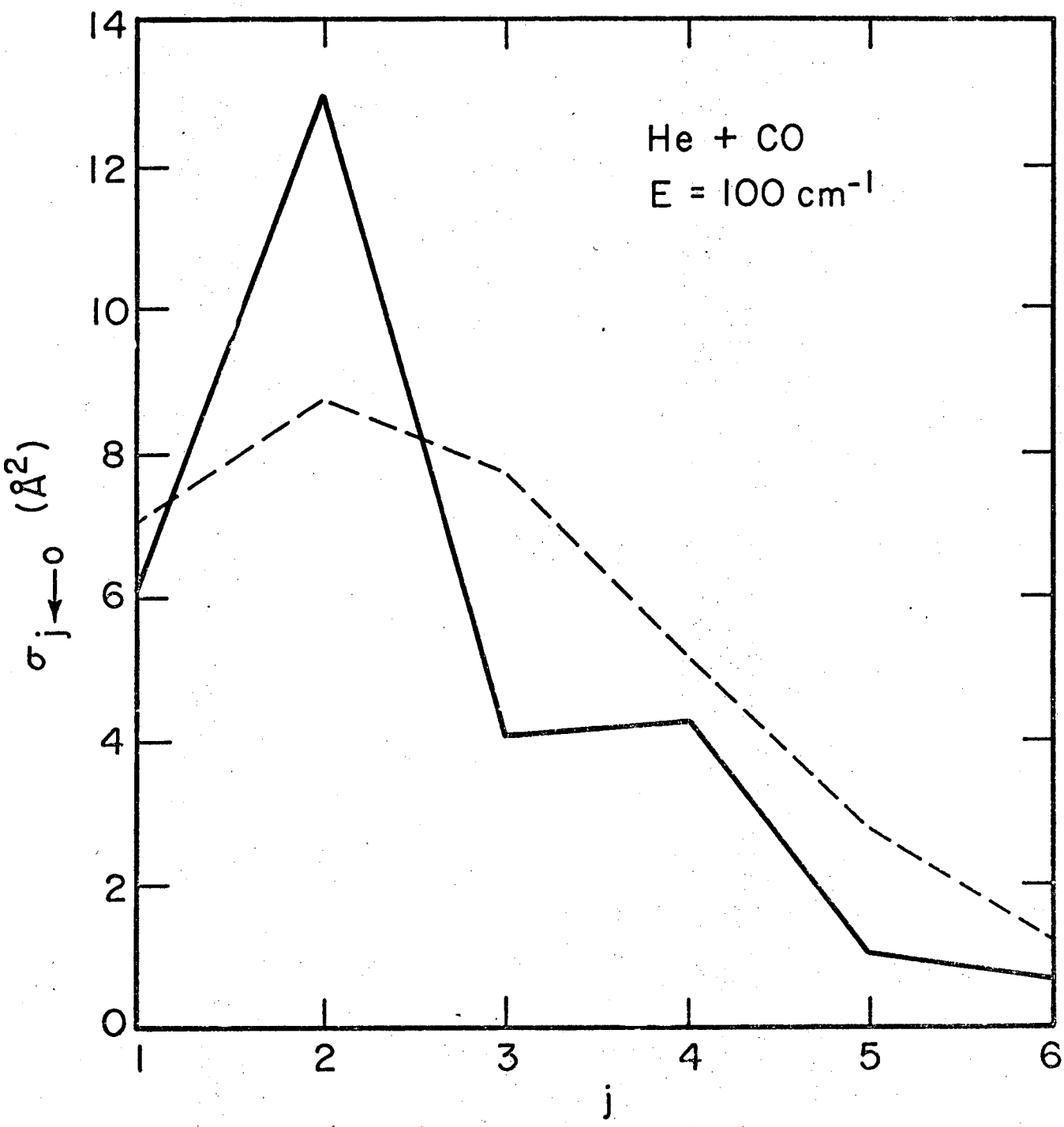

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Fig. 3

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