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Deconvolution of Molecular Beam Inelastic Scattering Data*

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Abstract

Two deconvolution techniques and their application to large angle scattering of molecular beams are considered. The first method, an interative unfolding (IU) technique due to Ioup and Thomas, is shown to contain an error; this error is corrected, but still further limitations are shown to exist. The second deconvolution method, which involves a folding-together of apparatus and assumed scattering functions, is used to analyze some data previously analyzed by the IU method. The new results in every case show that average (vibrational) inelasticities were overestimated both by analysis of the scattering results without deconvolution and by application of the IU method. The reason for the original overestimate is quite general and is easily understood. A simple classical theory agrees reasonably well with the new energy transfer values over a wide range of collision energy.

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† Miller Fellow

I. Introduction

To interpret molecular beam scattering data meaningfully one invariably finds it necessary to transform the laboratory intensities to the center-of-mass (c.m.) coordinate system. If there were no broadening of the laboratory data due to beam energy and angular spreads and due to detector bandpass, then there would exist a uniquely determined velocity $\vec{w}'$ relative to the c.m. for each laboratory product velocity $\vec{v}'$. This would allow an easy transformation of any laboratory differential cross section $\frac{d^3\sigma}{d^2\Omega dv'}$ to the corresponding c.m. differential cross section $\frac{d^3\sigma}{d^2\omega\, dw'}$ using the Jacobian transformation[1-3] $\frac{d^3\sigma}{d^2\omega\, dw'} = \frac{w'^2}{v'^2}\frac{d^3\sigma}{d^2\Omega\, dv'}$, where $\omega[=(\theta,\phi)]$ and w' are the c.m. angle and velocity directly corresponding to their laboratory counterparts $\Omega[=(\Theta,\Phi)]$ and v'. With apparatus broadening, however, the non-unique c.m. location adds considerable difficulty to the data inversion from laboratory to c.m., since a specified laboratory velocity $\vec{v}'$ corresponds to a range of c.m. velocities $\vec{w}'$. As a first step, the data can be removed from the laboratory coordinate system (where volume elements have sizes proportional to v'^2) by dividing laboratory flux-velocity intensities by v'^2. This technique, first employed by Mahan and co-workers[4] and later clarified by some of its advocates,[5,6] produces a differential cross section ($\bar{I}$) relative to a cartesian coordinate system[7] with many inherent advantages over laboratory coordinates.[5,6] Yet, failure to account for apparatus broadening effects in this cartesian presentation may still lead one to significant errors in interpretation of scattering results; deconvolution techniques are necessary to assure a proper interpretation of the data.

The most widely used deconvolution method[7-9] assumes a c.m. functionality and integrates over the laboratory variables to produce a broadened laboratory contour map corresponding to the chosen c.m. function. Comparison of the results with the laboratory data usually allows one to improve the guess on the next iteration. In favorable cases extensions of this "integration-fitting" (IF) method to a general least-squares fitting procedure[10-12] have aided the process of convergence to a suitable c.m. differential cross section functionality.

A less general one-dimensional iterative-unfolding (IU) method[13] has been used on energy profiles of reactive[14] and inelastic[15] 0° and 180° (c.m.) scattering resulting from an ion beam passing through a chamber containing a target gas.

This paper points out an error in the application of the IU[13] method to molecular scattering data and discusses corrective measures and their limitations. Some representative inelastic 180° backscattering data of Mahan and co-workers[15] are then deconvoluted using the IF techniques of Warnock and Bernstein.[8] The expected narrowing of the intensity distribution functions is accompanied by a significant decrease in the average excitation transfer relative to the results derived without deconvolution; the origins and implications of this shift are discussed, along with a modification of the classical impulse approximation which yields reasonable agreement with the altered results.

II. One-Dimensional Iterative-Unfolding (IU) Method

Consider an ion beam (A^+) of nominal energy E_o with a laboratory energy profile P(E) passing through a scattering gas BC. Let $H(E_z)$ be the measured laboratory energy profile of product (AB^+) in the same direction as A^+ (the z direction); this distribution contains the desired differential cross section F(E) broadened by apparatus effects. Let $G(E_z-E)$ be the function which correctly describes the contribution to the measured signal at energy E_z by particles which actually have laboratory energy E; then the measured signal at E_z is given by

$$H(E_z) = \int_{-\infty}^{\infty} F(E)G(E_z-E)dE \equiv F*G , \qquad (1)$$

the convolution of F with G.[16] If G is known, this equation may be solved for F(E) by first smoothing the data,[17a] then applying van Cittert's[17b] iterative deconvolution technique.[13]

The function $G(E_z-E)$ depends in a complicated way on apparatus resolution functions and reaction kinematics; Ioup and Thomas[13] assumed that $G(E_z-E)$ in Eq.(1) could be replaced by $P(E_z-E)$, the measured primary beam profile shifted from the nominal beam energy E_o to an origin E_z, and that all broadening effects from the primary beam and detector bandpass (but not from the scattering gas) could be thereby removed. By means of a simple example, we will now show that their assumption can introduce significant error in the deconvolution.

We wish to evaluate the effective shift $\Delta E'$ (hereafter, primed symbols refer to "after the collision;" unprimed, "before") in the

laboratory energy of scattered product that is associated with a change ΔE_o in the ion beam energy. It is therefore instructive to consider a reactive scattering event $A^+ + BC \rightarrow AB^+ + C$ where the BC velocity in the laboratory is initially zero (with no spread) and where the scattered AB^+ is produced at a particular total relative (c.m.) energy E_R' (with no spread). Then (in the assumed one dimensional situation) the entire width $\Delta E'$ in the laboratory energy of scattered product is due to the corresponding ion beam width ΔE_o. The laboratory energy E' at which reactive scattering of fixed final relative energy E_R' will be located can easily be computed:

$$E' = m_{AB}\left[\left(\frac{m_A E_o}{M^2}\right)^{1/2} \pm \left(\frac{m_C E_R'}{m_{AB} M}\right)^{1/2}\right]^2$$

where E_o is the ion beam energy, $M = m_A + m_B + m_C$, and the + and - signs refer to 0° and 180° c.m. scattering, respectively, here and below. A shift of ΔE_o in beam energy then causes a corresponding product shift

$$\Delta E' = \left[\frac{m_{AB} m_A}{M^2} \pm \left(\frac{m_{AB} m_A m_C}{M^3} \frac{E_R'}{E_o}\right)^{1/2}\right] \Delta E_o \quad . \qquad (2)$$

By replacing $G(E_z-E)$ by the shifted beam profile $P(E_z-E)$, Ioup and Thomas[13] in effect presupposed a constant broadening (independent of E_R') due to the ion beam spread; and their application of Eq.(1) is equivalent to the assumption that $\Delta E' = \Delta E_o$ for all values of E'. As Eq.(2) demonstrates, the correct relation is a complicated function of masses and energy, differs for forward (0°) and backward (180°) scattering, and furthermore varies for different values of E_R'.

A modified deconvolution procedure can be developed by considering a parallel development in velocity space. Let the ion beam (A^+) have laboratory velocity v_o (with spread Δv_o), let the laboratory velocity of BC be zero initially, and consider AB^+ produced at a specified c.m. velocity w'. Then the final laboratory velocity of AB^+ is given very simply by

$$v' = \left(\frac{m_A}{M}\right)v_o \pm w' \tag{3}$$

with the first term equal to the laboratory velocity of the centroid. The spread in product laboratory velocity $\Delta v'$ is related to Δv_o by

$$\Delta v' = \left(\frac{m_A}{M}\right)\Delta v_o \ , \tag{4}$$

where $\Delta v'$ is equivalent to the centroid motion caused by Δv_o and does not depend on w', v_o, or product masses. Hence, with velocity as abscissa the approach to be followed is clear; the ion beam velocity spread profile $P(v)$ is narrowed by the mass factor $\left(\frac{m_A}{M}\right)$ and this narrowed distribution is then used in the iterative deconvolution.[13]

This altered deconvolution approach also allows an equivalent removal of the broadening caused by the scattering gas: with a BC velocity v_z in the z direction, a centroid-motion term $\left(\frac{m_{BC}}{M}\right)v_z$ is needed in Eq.(3) and the scattering gas velocity profile can be analogously narrowed by the factor $\left(\frac{m_{BC}}{M}\right)$ with deconvolution then proceeding as above.

III. Difficulties Remaining in Improved IU Deconvolution

The detector bandpass function causes a minor complication when treated as part of the primary beam profile. The difficulty is due to the measured ion beam profile P(v) being itself a convolution of the true ion beam profile B(v) with the detector bandpass function D(v). The width of the D(v) function $\Delta D(v)$ frequently depends[5] on v (e.g., $\Delta D(v)$ is proportional to the velocity v for all electrostatic and magnetic deflection analyzers); hence the broadening of the scattered signal caused by the detector bandpass will vary with velocity and will generally be different from the D(v) appropriate to the ion beam profile. The narrowed function $B\left(\frac{M}{m_A} v\right)$, if it can be extracted from P(v), should be used in deconvoluting the effects of the ion beam; then the broadening of the scattered signal associated with detector bandpass could be removed separately in a slightly modified deconvolution procedure. If D(v) can be reasonably estimated, this complication is in theory surmountable.

However there are still two remaining difficulties associated with the one-dimensional IU method, both of which severely limit its possible applicability.

1) The major shortcoming of the method is its "restriction" to one-dimensional deconvolution;[18] in most ion-beam scattering profile experiments, velocities normal to the ion beam direction cannot be neglected when quantitative information on energy transfer is desired. Observe that a one-dimensional equation (e.g., $w' = \frac{m_A}{M} v_o + \frac{m_{BC}}{M} v_2 - v'$)

relating w' (and thereby internal energy transfer) to v_o, v_2, and v' corresponds to a lower bound to w'; this is because it replaces all vector velocities ($\vec{v}_o$, $\vec{v}_2$, $\vec{v}'$, $\vec{w}'$) by their components along the z axis. Consideration of <u>any</u> normal velocity components (associated with ion beam, scattering gas, or allowed detector acceptance) would effectively increase $|w'|$. The one-dimensional assumption then <u>always</u> overestimates the internal energy residing in the product molecules (and, parenthetically, slightly underestimates the average relative collision energy); the size of the error can be determined through use of a deconvolution method only if the method accounts for the normal velocity components.

2) The second problem with the IU method is a more subtle one involving a limitation on the possible functional forms for the deduced differential c.m. cross section. In order to develop that limitation, suppose that, at a specified relative collision energy E_R, the c.m. scattering has a functional form $F(E_R';E_R)$ and the products have average internal excitation $\overline{U}'$. Define the collision exothermicity Q by $Q \equiv E_R' - E_R$, the gain (or loss) in relative translational energy. Then $Q = \Delta D_o + U - U'$, where ΔD_o is the ground state exothermicity of reaction (equal to zero for non-reactive scattering) and U, U′ are the internal energies of reactants and products, respectively. The total energy available to the products, $E_{tot} = E_R + U + \Delta D_o$, is partitioned between E_R' and U'. Next, consider what variations in $F(E_R';E_R)$ and $\overline{U}'$ are possible when one varies the collision energy from E_R to $E_R + \Delta E_R$. The possibilities are, of course, limitless and only three simple cases will be illustrated here.

a) $F(E_R'; E_R + \Delta E_R) = F(E_R'; E_R)$; $\Delta U' = \Delta E_R$

This case corresponds to putting all of the excess collision energy ΔE_R into product excitation; a plot of $\bar{U}'$ (or -Q) vs. E_R would have a slope $-\frac{dQ}{dE_R}$ of unity at the initial relative energy considered. With no dependence on E_R, the c.m. function can be written in the simpler form $F(E_R')$.

b) $F(E_R' + \Delta E_R; E_R + \Delta E_R) = F(E_R'; E_R)$; $\Delta\bar{U}' = 0$

This is another limiting case and assumes that any excess collision energy ends up as excess product relative energy with no additional internal state excitation. The plot of $\bar{U}'$ vs. E_R has zero slope; collisional exothermicity is preserved and the c.m. cross section function can be written in another way: $F(Q; E_R + \Delta E_R) = F(Q; E_R) \equiv F(Q)$, where $F(Q)$ is invariant to changes in the collision energy.

c) $F(E_R' + \frac{E_R'}{E_{tot}} \Delta E_R; E_R + \Delta E_R) = F(E_R'; E_R)$; $\Delta\bar{U}' = \frac{\bar{U}'}{E_{tot}} \Delta E_R$

In this instance the quantity conserved is f, the fraction of total product energy residing in internal states of the product. If we define $f \equiv U'/E_{tot}$, then the equivalent c.m. function $F(f; E_R + \Delta E_R) = F(f, E_R) \equiv F(f)$ does not change as the collision energy is varied. A plot of $\bar{U}'$ vs. E_{tot} ($= E_R + U + \Delta D_o$) would have a slope $\bar{U}'/E_{tot}$ at collision energy E_R.

The three functions $F(E_R')$, $F(Q)$, and $F(f)$ were defined to be equivalent at a specified initial related energy E_R, with differences appearing only as the collision energy is varied about this nominal value. Which function gives a better approximation to the true variation

with incident energy depends upon the reaction being considered, and indeed, none of the three may be entirely satisfactory. Yet, a limitation in flexibility of the IU method is still apparent. The deconvolution, in treating $F(v')$, produces the narrowed c.m. function $F(w')$ [or equivalently $F(E_R')$] which contains no dependence on initial relative energy (this fact can be demonstrated by careful consideration of the convolution equation). The deconvolution cannot even be altered to produce $F(Q)$ or $F(f)$ or any other function which varies with incident collision energy. The reason is that, with two beam distributions, a given centroid velocity cannot uniquely specify an initial relative collision energy (recall that the convolutions have been shown to be equivalently represented by centroid motions in velocity space). The IU deconvolution then necessitates the assumption of no incident energy dependence over the range of collision energies possible in a given experiment. While analysis of experiments performed at several initial energies may indicate how a scattering function does depend on initial relative energy, it is not possible to extract this information from any one experiment, or conversely to use any such auxiliary information in the interative deconvolution.

The above two difficulties, associated with neglect of normal velocity components and inflexibility of functional form, are readily overcome when one uses the alternate and more general integration-fitting method.

IV. Integration-Fitting (IF) Deconvolution Method

A. General Comments

The calculations to be described here are analogous to the integration-fitting (IF) deconvolution methods of Warnock and Bernstein.[8] A c.m. differential cross section functionality is first assumed and the corresponding laboratory intensity distribution is then determined by a properly weighted multi-dimensional integration over the beam velocity vector distributions and detector acceptance function. The calculated laboratory intensities are then compared with the experimental data, and another c.m. function is tried in an attempt to improve the calculated fit to the data. The goal is a differential c.m. cross section functionality that, when averaged over all apparatus broadening effects, gives a good fit to the experimental data.

Several general observations on the procedure need to be emphasized.

1) For computational efficiency one may try many assumed c.m. functions simultaneously; this is particularly valuable at the start when little may be known except qualitatively, about the effects of the broadening.

2) In the integrations any known apparatus spread can in principle be included; in particular, one can account for the effects of normal velocity components in nominally "one-dimensional" energy profile experiments.

3) Apparatus broadening known to exist, but which has not been directly measured, can be estimated and then integrated in an approximate

way. Uncertainties in the approximation would lead to possible systematic errors in the deconvolution; yet these errors are usually much smaller than those associated with completely neglecting the uncharacterized spread.

4) One may also make any simplifying assumptions justified by the data or by supplementary information. Initially simple functional forms are assumed, but if the data are of high quality and the beam distributions are well characterized, more complex functions can be tried. In particular, any dependence [$F(E_R')$, $F(Q)$, $F(f)$, ...] on incident relative energy may be assumed and the effects of the resultant assumptions compared.

5) In some cases the data may be reliable enough to justify an extension of the IF method to a more general least-squares fitting procedure; this has been used and described elsewhere.[12]

6) Finally, some mention must be made of the problem of uniqueness. There is obviously only one true c.m. cross section functionality for an experiment; nontheless, there may be a range of trial functions which reproduce the data within experimental error. The calculational process should <u>ideally</u> emphasize the discarding of unacceptable functions, but, in practice, one hardly ever does more than to try to find a satisfactory fit to the data.

More importantly, different calculational assumptions (e.g., dependence on initial collision energy) may yield quite different final results. A "satisfactory" function is only satisfactory if all of the initial assumptions are known to be reasonable, and it is therefore

quite important to specify the assumptions involved in the deconvolution attempt (see section C below).

B. Apparatus Summary

The apparatus and the data acquisition techniques have been described in detail previously.[5,15] Briefly, ions from a microwave discharge source are momentum analyzed by a magnetic mass spectrometer and focused to produce a nearly parallel ion beam of circular cross section with a typical (measured) angular spread of 1.5° FWHM (full-width at half-maximum) and energy spread of 3% FWHM. The ion beam enters a scattering cell filled with He; inelastically scattered products are analyzed by a 90° spherical electrostatic energy analyzer and a quadrupole mass spectrometer and are then counted.[5] The detection system has circular aperture geometry, an angular FWHM of ~1.5°, and an energy FWHM of ~3% of the energy nominally transmitted.

C. Calculational Assumptions and Functional Forms

1) All deconvolutions discussed here consider only "backward" inelastically scattered ions (detected in the direction of the original ion beam, but at laboratory velocities lower than the original centroid velocity).

2) Cylindrical symmetry is assumed for the beam and for the detector system, since most of the defining slits are circular (one is square) and most focusing elements have cylindrical or "quadrupole" symmetry.

3) In the IF convolutions one of the integrations is over the velocity distribution of the ion beam, B(v); yet the measured ion beam profile P(v) is itself a convolution of B(v) with the detector transmission function D(v). The function B(v) is obtained from P(v) by an IU deconvolution calculation[19] using a reasonable estimate for D(v).

4) For velocities normal to the ion beam direction, approximate Gaussian width parameters σ were calculated (scattering gas parameter calculated trivially from its temperature, detector acceptance angles calculated from detector geometry, ion beam angular widths estimated from measured beam angular profiles). Integrations over normal velocity components were done by spacing and weighting the integration points with a modified Gaussian distribution function $\frac{v}{\sigma} \exp -\left(\frac{v^2}{2\sigma^2}\right)$.

5) A simple two parameter Gaussian functional form was assumed for the differential cross section function, e.g. $F(Q) = e^{-(Q-Q_o)/2\rho^2}$ where Q_o is the nominal exothermicity of the reaction (for "backward" 180° c.m. scattering) and ρ is a measure of the range of Q values. This functional form was chosen in order that the calculations should concentrate on extracting the most essential information on the inelastic 180° scattering – the range of inelasticity and the average energy transfer – without laboring excessively to extract finer details than the quality of the data would warrant. For each experiment, a series of trial and error convolutions was made until the choice of (Q_o, ρ) gave satisfactory agreement with the data.

Some additional comments are necessary on the choice of functional form. First, since the existence of sizeable normal velocity components

causes nominally 180° backward scattering to contain many scattering events of somewhat smaller c.m. angle (down to ~160°), then the chosen differential cross section functionality assumes implicitly a lack of dependence of Q_o and ρ on scattering angle over the small range of angles accepted by the detector. Experimentally determined angular distributions[15] do indicate that the angular variations of Q_o and ρ are relatively small in the systems treated here.

Second, the incident energy dependence of the cross section functionality was not restricted to the form implicit in F(Q) [see section III]; slightly altered Gaussian forms consistent with the incident energy dependence associated with both $F(E_R')$ and F(f) were also used.

D. Results

1. $Ar^+(He,He)Ar^+$

In the limiting case of elastic 180° c.m. scattering data a satisfactory deconvolution technique would be expected to remove all apparatus spread and to produce a very sharply peaked c.m. differential cross section function centered at the elastic exothermicity value Q = 0.

Two very reliable Ar^+ + He 180° scattering experiments (both having stable and well characterized ion beam distributions) were deconvoluted and yielded very similar and highly satisfying results. One of these experiments is shown in Fig. 1. Since reaction exothermicity Q is inherently more interesting than product velocity v, each laboratory velocity has been converted (using the nominal ion beam velocity) to its associated Q value; the data intensities (in the cartesian differential

cross section representation $\bar{I}$[5,6]) are plotted against the abscissa Q. These data are matched quite well by the calculated points which were generated by convoluting the function F'[20] with the known apparatus resolution functions. For pure elastic scattering the c.m. cross section function should be of infinitesimally small energy width and should be centered at Q = 0. Function F'[21] has an average exothermicity $\bar{Q}$ = -0.1 eV and a width parameter ρ = 0.1 eV; both the average endothermicity and the range are quite small compared to the uncorrected data ($\bar{Q}$ = -0.6 eV, energy FWHM ~3.4 eV). The remaining small endothermicity is comparable to that associated with the electronically inelastic channel of Ar^+ ($^2P_{3/2} \rightleftharpoons {}^2P_{1/2}$ -0.18 eV), an inelastic channel undoubtedly available to the system. Yet, even without invoking the possible inelastic channel, we conclude that the small deviation from the ideal elastic expectation is easily within the range of possible drifts in ion beam energy during the experiment. The deconvoluted results are in excellent agreement with our expectations for this system.

The three-dimensional deconvolution not only demonstrates the expected shift to more positive $\bar{Q}$ (in this case from -0.6 to -0.1 eV), but also produces a dramatic narrowing in the range of Q. This success with "elastic"[22] scattering indicates that the methods are analogously applicable to true inelastic scattering experiments.

2. $O_2^+(He,He)O_2^+$ and $NO^+(He,He)NO^+$

A representative result of IF deconvolution applied to inelastic backscattering can be seen in Fig. 2; in this example the differential cross section function F'[20] was chosen to have an incident energy

dependence corresponding to $F'(f)$. Also determined were the best functions of form $F'(Q)$ and $F'(E_R')$; the relevant parameters for all three functions are given in Table I. For inelastic 180° scattering in the systems $O_2^+(He,He)O_2^+$ and $NO^+(He,He)NO^+$ the incident energy dependence implied by $F'(f)$ gives the best approximation to the true slope $-\frac{d\bar{Q}}{dE_R}$ of a plot of inelasticity vs. relative energy for experiments over a wide range of collision energy (this can be seen in Figs. 4 and 5 below). Hence $F'(f)$, as in Fig. 2, is the best choice of c.m. differential cross section incident energy dependence for the reactions being considered here. Note that the choice of energy dependence has very little effect on the average energy transfer $|\bar{Q}|$; note also, that (as expected) $|\bar{Q}|$ is significantly less than the result for one-dimensional IU deconvolution.[15] The correction due to normal velocity components is ~0.4 eV in this case; an additional 0.1 eV arises from converting to the differential cross section $\left(\frac{d^2\sigma}{d\theta\ dE'}\right)$, which is the one appropriate for correctly determining energy transfer probabilities.[20]

Figure 2 also indicates $D(O_2^+)$, the dissociation energy of O_2^+. The deconvolution is successful in removing intensity in the forbidden region corresponding to O_2^+ excited beyond its dissociation limit. Intensity with positive Q values (de-excitation) is, however, still evident after the deconvolution; this is actually quite reasonable since the original O_2^+ can have significant vibrational excitation (the average excitation has been estimated to be ~0.3 eV) prior to collision.

A deconvoluted result for $NO^+(He,He)NO^+$ is shown in Fig. 3; the conclusions drawn are quite similar to those for the O_2^+ + He system.

3. Shift in Average Energy Transfer

Seven other inelastic 180° results of Ref. 15 have been deconvoluted[23] and have yielded results comparable to those described above. Generally the average energy transfer $|\bar{Q}|$ has been decreased by 10-30% relative to the original conclusions and the width parameter has been narrowed by 20-40%.

E. Discussion

The decrease in energy transfer is the most interesting result of these calculations, since it removes the reasonable agreement between the experiments of Ref. 15 and the calculations[15] based on Mahan's correction[24] of classical vibrational excitation theory.[25] Figures 4 and 5 demonstrate the new results where the average endothermicity $-\bar{Q}$ is plotted against collision energy for a series of experiments. It is clear that the deconvoluted results yield energy transfer values which are significantly lower than the refined impulse approximation (RIA) calculations of Ref. 15. However, there is an additional correction[25] that must be applied to the classical RIA formulation before it can be reconciled with exact quantal results. One should compute the energy transfer for an <u>effective</u> relative collision velocity which is an average of initial and final values.[26,27] This correction, by symmetrizing the collision, attempts to extract an average energy transfer consistent with detailed balance considerations. In practice, the energy transfer ΔE is calculated (using Eq.(4) of Ref. 15) for an energy E_o; then values of E_R and E_R' are found which satisfy the following:

$$E_R^{1/2} + E_R'^{1/2} = 2E_o^{1/2} \quad \text{(velocity averaging)}$$

and $$E_R - E_R' = \Delta E.$$

A plot of ΔE (=-Q) against E_R[28] represents the velocity-averaged refined impulse approximation (VARIA); the relevant curves are given in Figures 4 and 5.

The agreement between the IF deconvolution results and the VARIA calculations is remarkably good for both system (in the NO^+ + He case, the VARIA "predictions" are assumed to be an average of the calculations for the two different orientations of the NO^+). Perhaps, if all of the O_2^+ + He data were considered (estimating expected shifts for those experiments which were not deconvoluted[23]), it might be concluded that the VARIA calculations slightly overestimate the average energy transfer to the O_2^+ oscillator. Yet, the set of data for NO^+ spans a greater range of E_R and has much less scatter than the O_2^+ data and is thought to be more reliable.

It is, of course, not difficult to locate experimental considerations which would be expected to decrease the measured energy transfer by small amounts relative to that predicted by the VARIA calculation:

a) The ions are partially excited (average excitations of a few tenths of an eV) and the calculation considers only ground state oscillators.[29]

b) The measured "180° scattering" really includes many inelastic events with lower scattering angle, due to finite apparatus resolution; the average scattering angle detected should be typically ~170° c.m.

c) The experimental conditions are not really at the impulse limit (see Ref. 15) even at the highest collision energies.

If the VARIA calculations were modified to account for these three effects, somewhat less energy transfer would result; however, the appeal of the classical calculation is its simplicity, and this could easily be lost in applying many minor modifications. The fact that the VARIA calculations match the experimental average energy transfer values so well is more interesting than the effects of any small corrections. It must be remembered that the calculations totally neglect any non-linear effects (anisotropy of the potential, non-zero impact parameter and angular momentum) and might not be expected to do nearly as well as they in fact do.

F. Angular Variation of the Inelasticity

Reference 15 also included inelastic scattering data and model calculations for scattering angles less than 180° c.m. The considerations discussed in this paper can be applied completely analogously. Average values of experimental inelasticities for $\theta_{cm} \neq 180°$ are expected to decrease due to three-dimensional deconvolution by amounts comparable to the results for 180°, while the simple classical theoretical formulations will also yield decreased excitations when use is made of the velocity-averaging assumption. The primitive modified wave number approximation of Ref. 15, when velocity-averaged, still appears to be a simple, convenient, albeit näive, model that successfully predicts inelasticities in these systems.

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Table I

$O_2^+(He,He)O_2^+$ Inelastic 180° Scattering at E_R = 11.1 eV
Best Gaussian parameters[a]

	Q_o(eV)	ρ(eV)	$\bar{Q}$(eV)	$-d\bar{Q}/dE_R$
$F'(E_R')$	-2.8_0	1.4_5	-2.6_7	1.0
$F'(f)$	-2.8_0	1.3_0	-2.7_0	0.26
$F'(Q)$	-2.8_0	1.2_0	-2.7_1	0

[a]The parameters for $F'(E_R')$ and $F'(f)$ have been nominally converted to equivalent Q values for comparison purposes.

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15. M. H. Cheng, M. H. Chiang, E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, J. Chem. Phys. 52, 6150 (1970); note that Eq.(3) of this reference should contain M_A in place of M_B in the numerator.

Note also that after Eq.(2) of this reference, $\Delta E/E_R$ should be 0.3385 and 0.4179 for the two orientations in NO^+-He impulsive collisions.

16. There is a subtle complication associated with this statement; $G(E_z-E)$ contains not only the detector acceptance function, but also contributions from spreads in the two beams. Even if the detector accepted only one energy (E_z), G(0) would still involve a convolution over beam velocity distributions as different portions of the c.m. differential cross section yielded scattering precisely at energy E_z. For simplicity of description, the multi-dimensionality of the convolution integration is left out of Eq.(1).

17. a) J. D. Morrison, J. Chem. Phys. 39, 200 (1963);
    b) P. H. van Cittert, Z. Physik 69, 298 (1931).

18. Multi-dimensional unfolding is theoretically possible, but much more time consuming and much more difficult in actual practice. Also, quite often beam profiles in three dimensions must be estimated; this could lead to uncontrolled instabilities and non-physical irregularities in the course of a general IU computation.

19. A. S. Werner, University of California Lawrence Radiation Laboratory Report UCRL-20363 (1971).

20. The function F′ corresponds to a differential cross section of the form $\frac{d^2\sigma}{d\theta dE'}$ $\left[\text{or really } \left(\frac{d\sigma}{dE'}\right)_{\theta=180°}\right]$ and is the proper functionality for determining the distribution of product internal states (see References 3, 12). F′ is generated from the deduced cartesian c.m.

function $\bar{I}_{cm} = F$ by using the Jacobian transformation $F' \propto w'F$; if left uncorrected, the function F would imply internal excitations somewhat larger than those associated with F'.

21. Although plotted vs. abscissa Q for the nominal collision energy considered, the function F' had an incident energy dependence corresponding to the fractional excitation function $F'(f)$ defined in Section III of the text.

22. The system is essentially elastic since the detector bandwidth (3% FWHM) was approximately ten times as large as the expected spacing ($^2P_{3/2} \rightarrow {}^2P_{1/2}$) of the Ar^+ levels; the deconvolution would not be expected to achieve resolution of transitions so close in energy relative to detector bandpass.

23. Although some of the experiments in Ref. 15 lacked sufficient beam characterization (specifically, ion beam angular distributions) to allow a full three dimensional deconvolution attempt, the results would not be expected to differ dramatically from those reported here.

24. B. H. Mahan, J. Chem. Phys. 52, 5221 (1970).

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26. a) K. F. Herzfeld, Thermodynamics and Physics of Matter, edited by F. D. Rossini (Princeton University Press, Princeton, N. J., 1955), Sec. H;

b) D. Rapp, J. Chem. Phys. 32, 735 (1960).

27. a) C. F. Hansen and W. E. Pearson, J. Chem. Phys. 54, 1539 (1971);

b) F. E. Heidrich, K. R. Wilson, and D. Rapp, J. Chem. Phys. 54, 3885 (1971).

28. In this nomenclature the RIA calculation would correspond to a plot of ΔE vs. E_o.

29. a) J. D. Kelley and M. Wolfsberg, J. Chem. Phys. 44, 324 (1966);

b) S. J. Yao and H. Y. S. Yao, J. Chem. Phys. 54, 4424 (1971).

Figure Captions

Fig. 1 A comparison of measured 180° c.m. $Ar^+(He,He)Ar^+$ data (△, solid line) with the calculated distribution (□) which was generated by convoluting the function F′ (dashed line) with apparatus broadening functions. The abscissa Q indicates the nominal Q values associated with each data point.

Fig. 2 $O_2^+(He,He)O_2^+$, inelastic scattering, similar to Fig. 1. Shown are data (△, solid line), calculated fit to data (□), and best c.m. function F′ (dashed line). The dissociation energy of O_2^+ is indicated by $D(O_2^+)$.

Fig. 3 $NO^+(He,He)NO^+$, inelastic scattering, similar to Fig. 2.

Fig. 4 A plot of average experimental and theoretical Q values for 180° scattering of $O_2^+(He,He)O_2^+$ as a function of relative energy, E_R. The original experimental data (○, ●) have been divided into two types: open circles (○) have not been corrected by deconvolution; closed circles (●) have been corrected and the (shifted) deconvoluted average energy transfer results are indicated by crosses (X) at the same incident energy.

The lines represent classical calculations of energy transfer: the hard sphere energy transfer prediction (Eq. 2 of Ref. 15) is represented by a dashed line; the

refined impulse approximation (RIA) prediction (Eq.4 of Ref. 15) is the upper solid line; and the velocity-averaged correction when applied to the RIA produces the lower solid line (VARIA).

Fig. 5 A plot of average experimental and theoretical Q values for 180° scattering of $NO^+(He,He)NO^+$ as a function of E_R. Similar to Fig. 4 with two exceptions:

1) Each of the theoretical calculations can be made with either of two alignments, $He\text{-}N\text{-}O^+$ or $He\text{-}O\text{-}N^+$; this generates a pair of curves for every approximation used. In each case the upper curve corresponds to $He\text{-}N\text{-}O^+$ (i.e., atom B = N).

2) For reasons of clarity, the RIA curves are not plotted for this system.

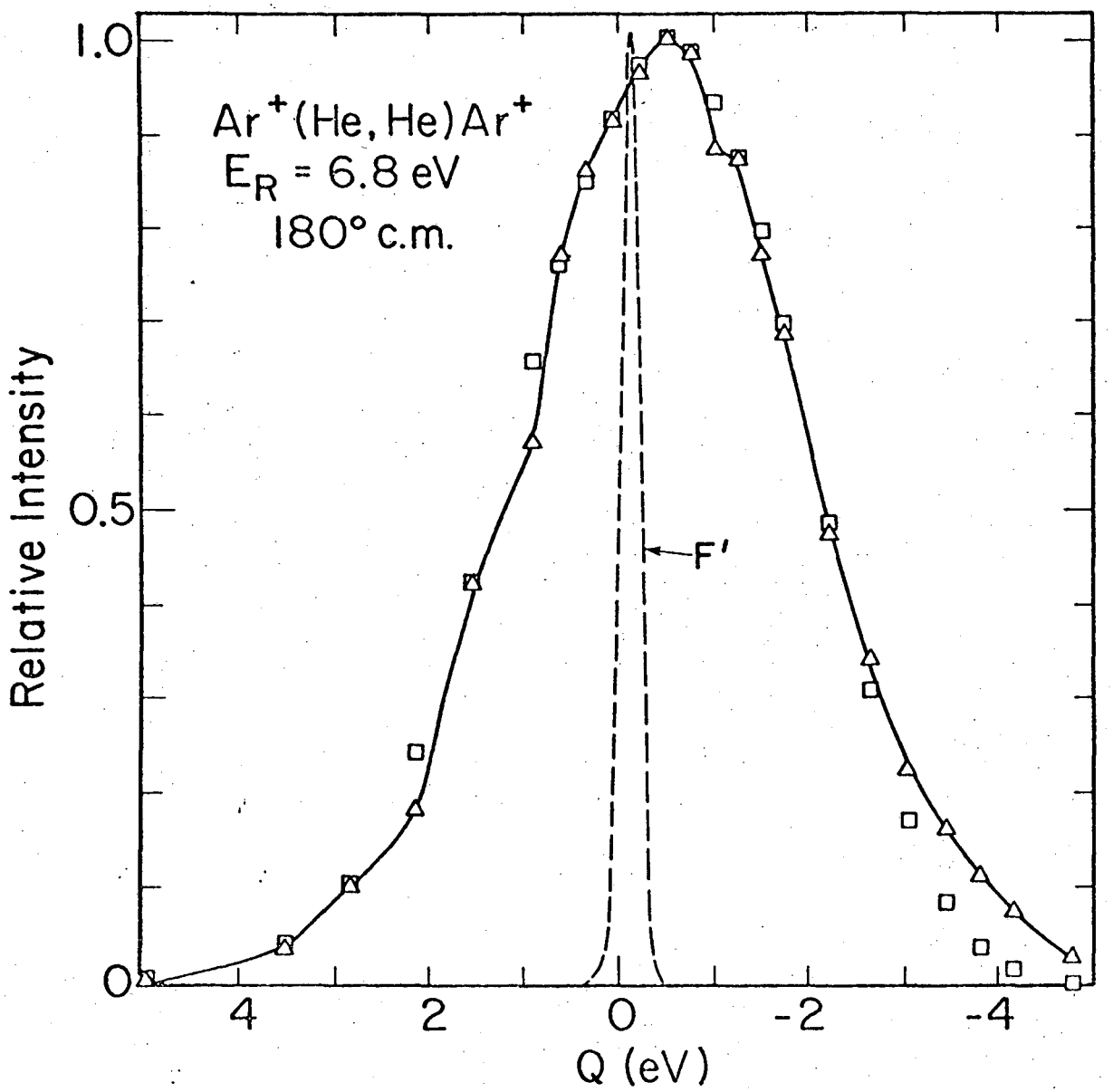
1.0
0.5
0
Relative Intensity
$Ar^+(He, He)Ar^+$
E_R = 6.8 eV
180° c.m.
F'
4
2
0
-2
-4
Q (eV)

Fig. 1

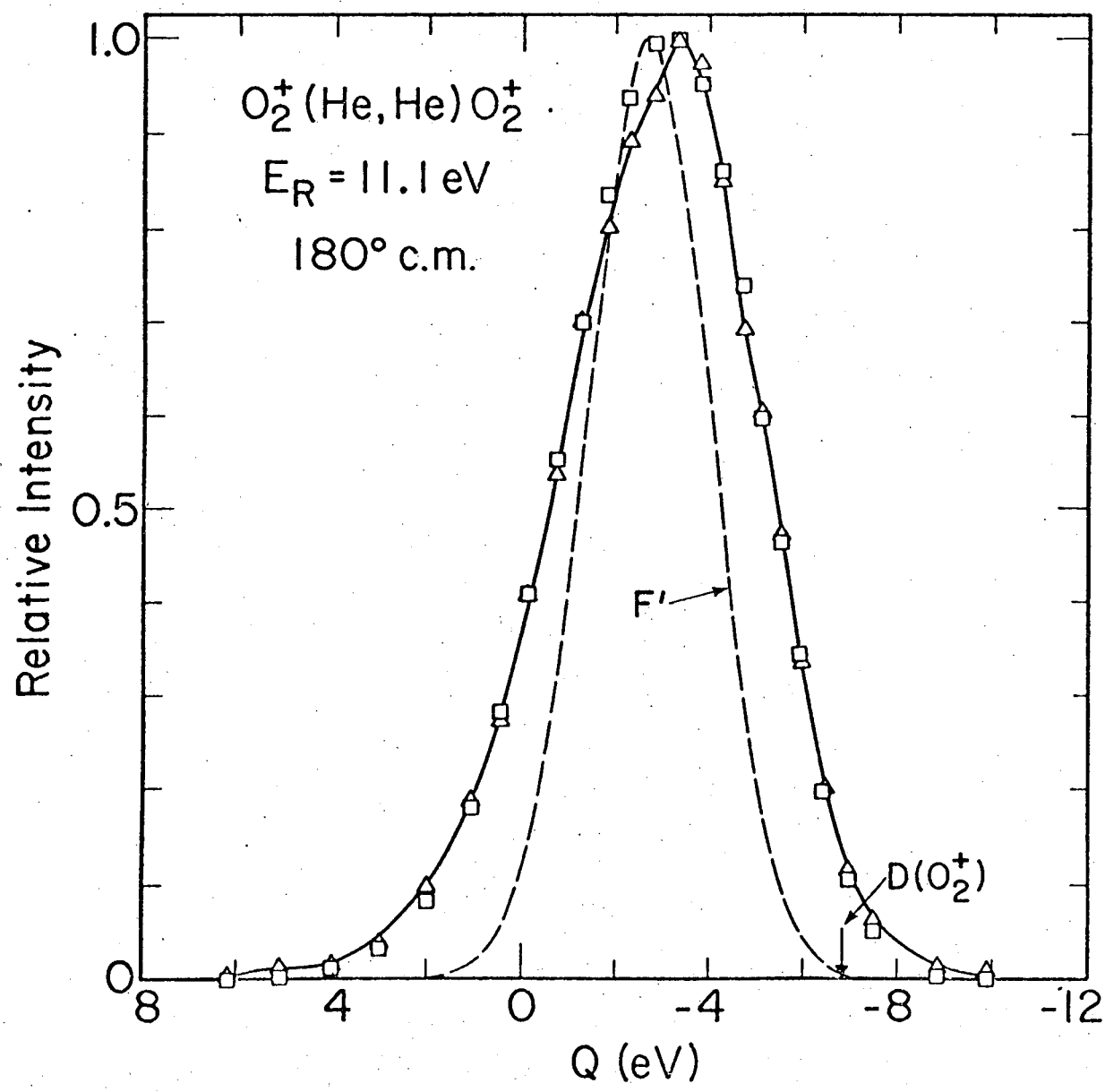
O_2^+(He, He)O_2^+
E_R = 11.1 eV
180° c.m.
Relative Intensity
1.0
0.5
0
F'
D(O_2^+)
8
4
0
-4
-8
-12
Q (eV)

Fig. 2

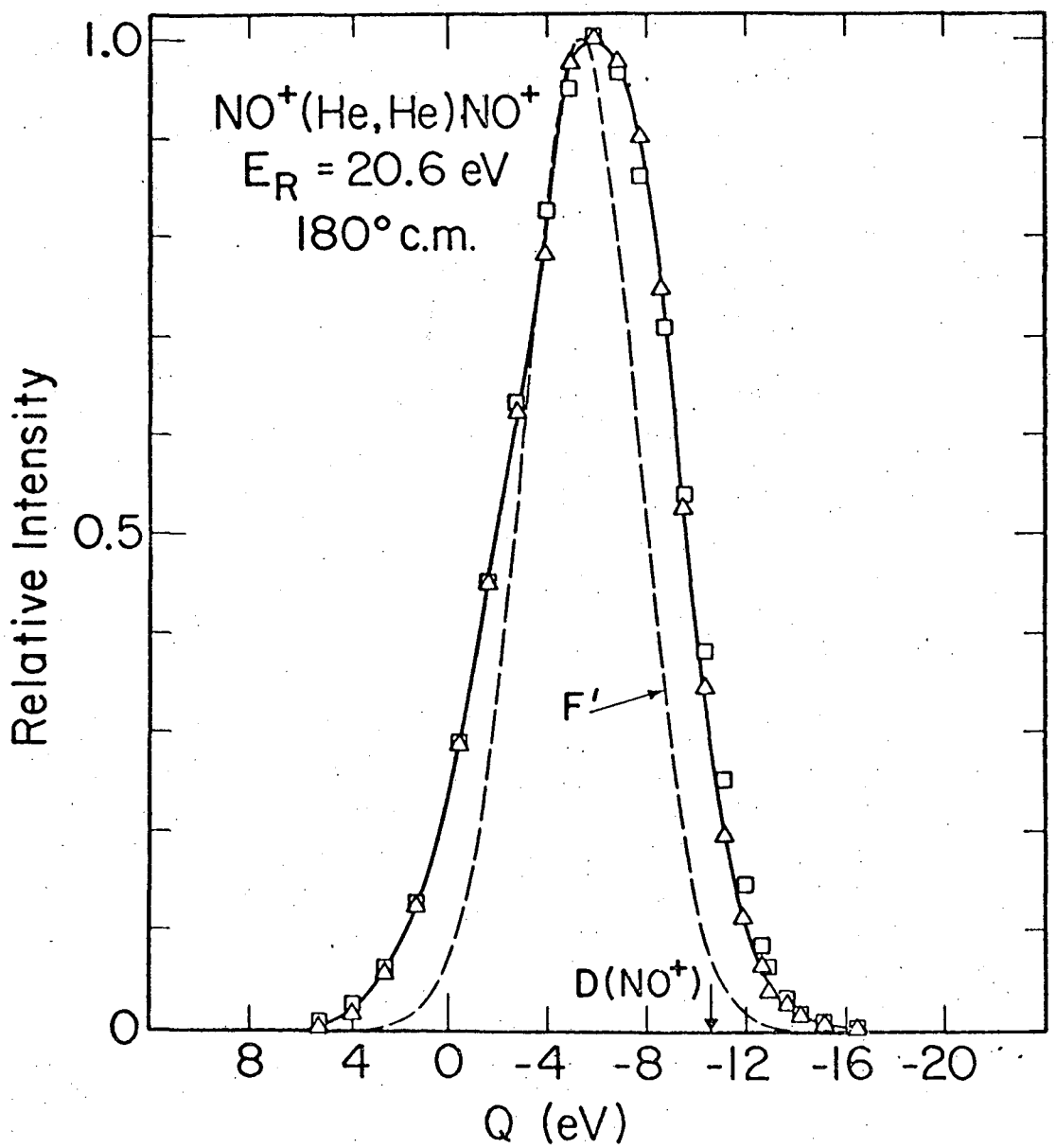
1.0
0.5
0
Relative Intensity
NO+(He,He)NO+
ER = 20.6 eV
180° c.m.
F'
D(NO+)
8
4
0
-4
-8
-12
-16
-20
Q (eV)

Fig. 3

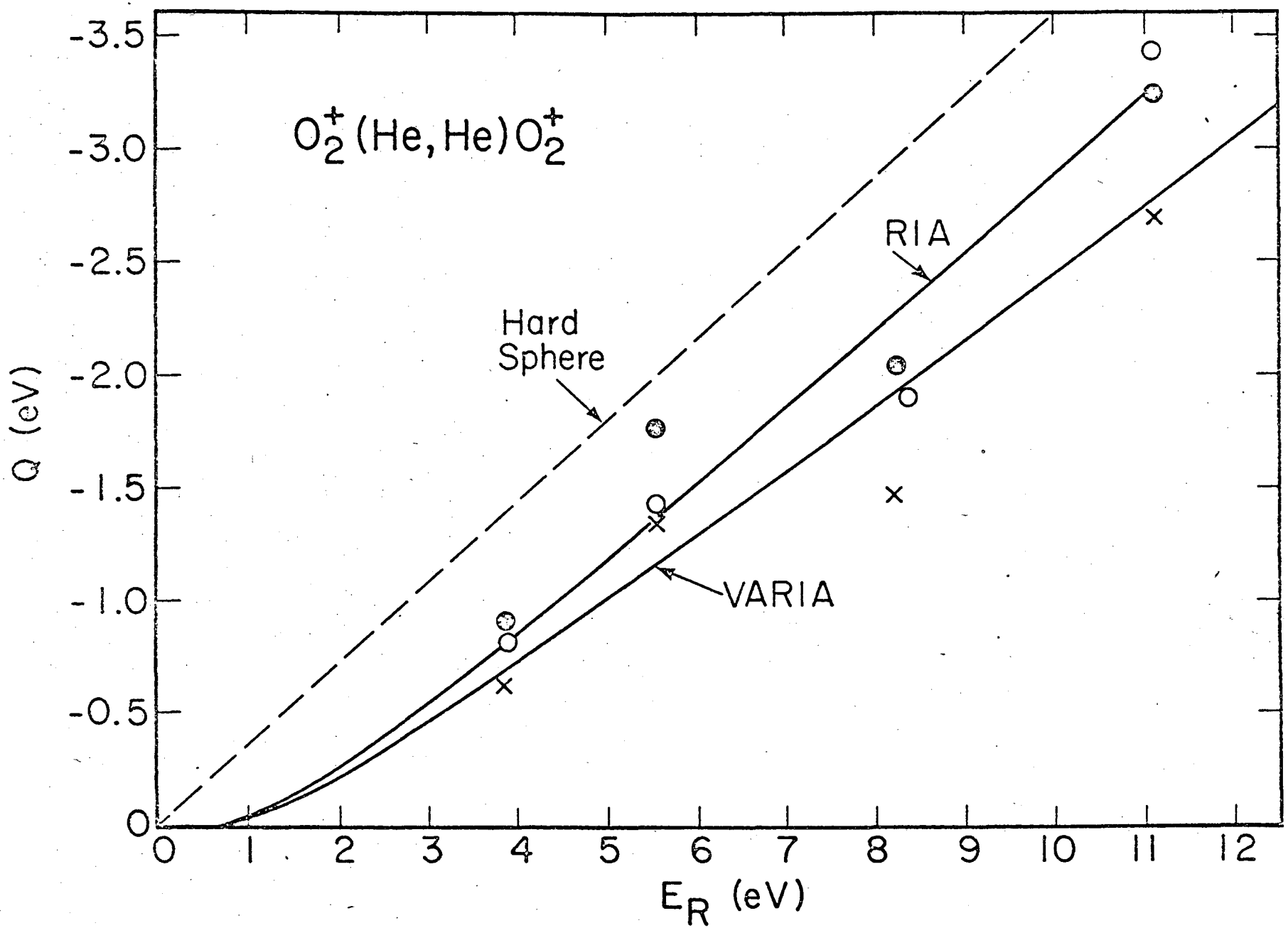
$O_2^+(He,He)O_2^+$
Hard Sphere
RIA
VARIA
Q (eV)
E_R (eV)
-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0
0
1
2
3
4
5
6
7
8
9
10
11
12

Fig. 4

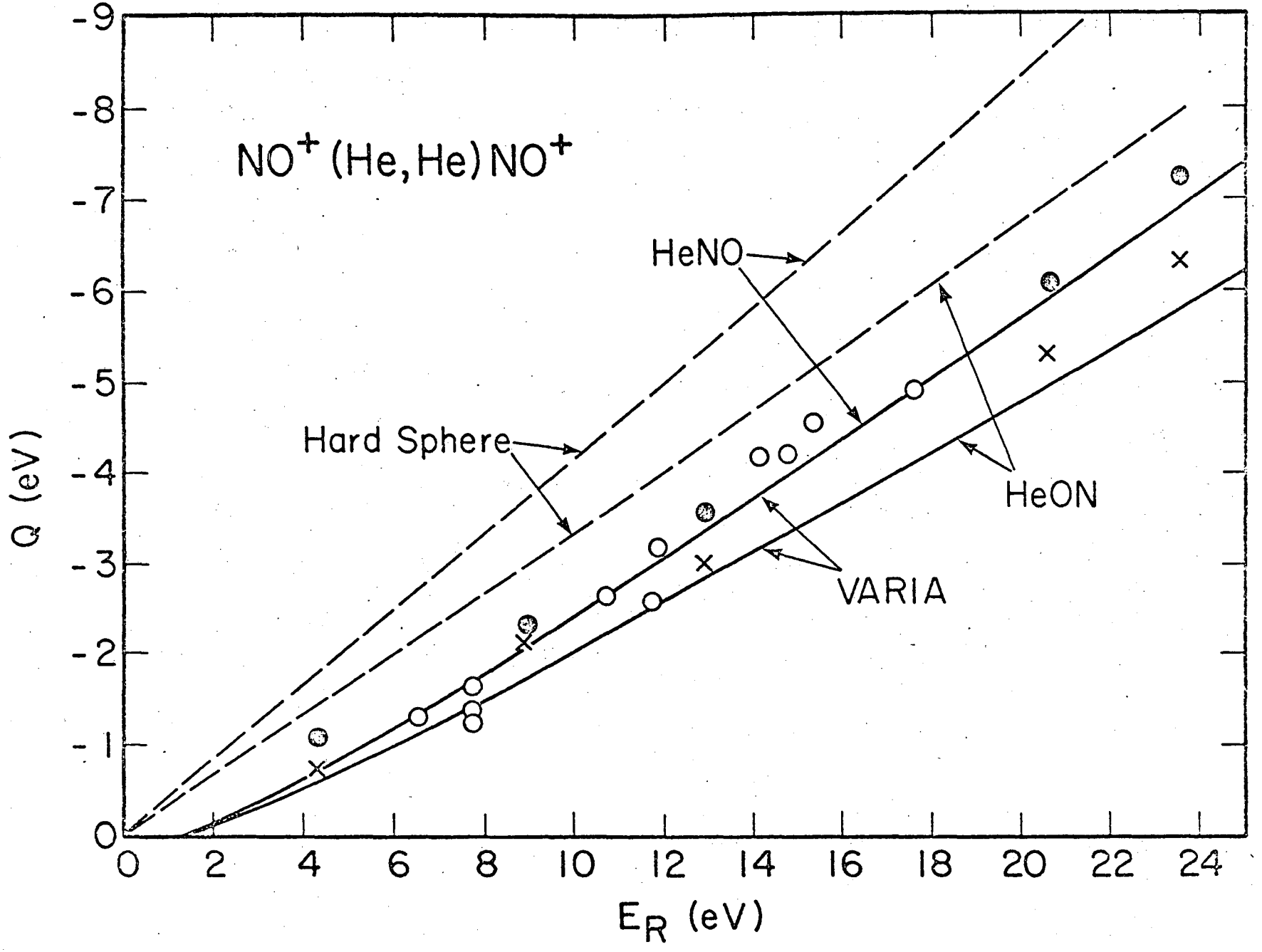
NO+ (He, He) NO+
HeNO
Hard Sphere
HeON
VARIA
Q (eV)
E_R (eV)
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
0
2
4
6
8
10
12
14
16
18
20
22
24

Fig. 5

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